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ANALYTICAL CHEMISTRY IN THE FORTHCOMING SEVEN YEARS

The plan for the development of the national economy of the USSR during 1959-1965, which has been accepted by the twenty-first session of the party, foresees a powerful increase in all branches of the economy of our country, as a result of which a decisive step forward will be made in creating the material-technical basis of communism. The plan has in view the rapid development of a number of the most important branches of the national economy, which will require the participation of analytical chemistry in organizing production control, preparing raw materials, and analyzing finished products. In this connection, analytical chemistry like all Soviet science is confronted by a number of serious, and, to a considerable extent, completely new problems.

The seven-year plan, and also the decisions reached by the May plenum of the Central Committee of the Communist Party of the Soviet Union in 1958, have in view, vast measures to be taken in order to speed up the development of chemical industry, particularly the production of synthetic and natural fibers, plastics, and other synthetics. The forthcoming years will see the "chemicalization" of the country. The total volume of production of the chemical industry will increase almost three times, while that of plastics and synthetic resins will increase 6-7 times. An important feature is that the polymer industry will develop on a new raw-material basis—natural gases and gases obtained as by-products of the petroleum industry. A number of the old branches of the chemical industry such as the production of nitrogeneous fertilizers, will also be based on the use of natural gas. There will be a considerable expansion in the chemical refining of petroleum.

The basic requirement, arising from these changes, which will confront analytical chemists will be to ensure the control of the production of polymeric and other synthetic materials. In this connection the question of considerably extending the work on functional chemical analysis arises. Attention must be focussed in particular on improving methods of analyzing mixtures of hydrocarbons. The ever increasing part played by, and the increase in production of elemental-organic compounds containing silicon, phosphorus, fluorine, and the other elements demand that new methods of analysis by developed for these compounds; work along these lines should, presumably, be concentrated in the same fields as synthetic investigations. The significant increase in attention which should be payed to the analysis of organic compounds is also connected with the necessity of finding methods for the determination of antibiotics and other biological materials. It should be ensured that wide use be made of physical and physicochemical methods of analysis for controlling the production of polymers.

Another important problem arising from the seven-year plan is the problem of the rare elements. The forthcoming years will be characterized by a sharp increase in the production of a number of rare elements, and by an increase in the sphere of their application. Analytical chemistry is confronted by the problem of giving more help to the industry of rare metals, and this help should not be limited only to organizing production control, although this will still remain the chief problem; analytical chemistry should participate in resolving problems connected with complex utilization of raw material, with the search for new sources of rare and scattered elements and intermediates, and studying waste products of various types, etc. The most advanced analytical schemes of separation may become the basis of new technological schemes.

It is essential that during the planning of new enterprises, more attention should be given to questions of production control, it being borne in mind that in a number of cases, the volume of work on control during the actual process may be cut down considerably as a result of organizing rational measures on conditioning the raw material. This is equally true for other branches of industry as well.

The problem which is always connected with the successes of a socialist economy and with the progress of technics, is the problem of determining trace impurities in various materials. This problem is of principal importance for the development of analytical chemistry as a science since it demands a new approach to analysis, and the development of original methods and equipment for analysis. One of the main fields of application in this connection will be the determination of impurities (down to 10^{-6}–10^{-8}%) in semiconductors, catalysts, and super-pure constructional materials; and determination of "micro elements" playing an important part in biochemical processes. Classical chemical methods which are not suitable for these purposes, will give way more and more to physicochemical and physical methods. Activation analysis, mass spectroscopy, and other modern methods will occupy an important place. The use of radioactive indicators which has been increasing in geometrical progression during recent years for the solution of analytical problems, will, in the forthcoming seven year, undoubtedly become even more important.

The wide and complex mechanization and automation of production processes envisaged by the seven-year plan, is of importance for analytical chemistry in the connection that there will be demands for a considerable increase in the development of chemical principles for automatic control and regulation of production. This is particularly important for the basic chemical, petroleum-refining, and gas industries. Of fundamental importance here will be the reasoned selection of properties and parameters suitable for automatic recording (light absorption, electrical conductivity, etc.), and the development of the appropriate apparatus (meters recorders). The use of instrumental physical and physicochemical methods should serve as a basis for automatic control.

Attention to the needs of ferrous and nonferrous metallurgy, the chemical industry, the mining industry, etc., and also of various branches of science will require further improvement of the classical methods of chemical analysis, and of chromatographic and extraction methods, coprecipitation, etc., which have come into wide use in recent years. From the practical point of view, work on speeding-up analysis and simplifying it is necessary in this connection. It must be emphasized that the problem of the speed of an analysis is a general one, important not only for factory control, but, also for example, for research with short-life radioisotopes.

The solution of all these problems which will arise as a result of the powerful technical progress foreseen by the seven-year plan, is impossible without a fundamental development of the technical basis of analytical chemistry. Naturally, the progress of analytical chemistry as a science is determined by two factors—on the one hand by the demands of life, and practice, and on the other hand by the internal laws of the development of universal analytical chemistry. In evaluating the basis scientific problems confronting analytical chemistry, it is necessary to take both factors into account.

Without doubt an important link in the development of the theoretical aspects is the study of reaction kinetics and mechanisms of analytical importance; here belong oxidation—reduction reactions, complex-formation, and hydrolysis, formation of precipitates, etc. In connection with the wide use of radiochemical methods in analytical chemistry, investigation of the behavior of ultra-small concentrations of materials in solution is becoming increasingly necessary. Of interest is the wider study of the properties of ions (energetic characteristics, etc), since these properties play, in essence, the decisive role in developing analytical methods for one element or another.

Development of the theoretical principles of chromatographic separation, and of coprecipitation, and of the theory of extraction separation of elements and compounds, is one of the real problems of science. There is a need for the development on a wider scale of the theoretical principles of the action of organic reagents for inorganic and organic analysis. The general tendency should be towards an increase in the quantitative sides of research, in particular towards the wider use of the methods of mathematical treatment of experimental results.

Of particular importance is a group of physicochemical and physical methods of analysis comprising, in particular, flame photometry, gas chromatography, oscillographic polarography, and also, hitherto not widely used methods such as electronic and nuclear magnetic resonance. More attention should be given to developing the principles of phase analysis, in which geochemistry, metal treatment, and other sciences are interested; in this connection it is desirable to use physical methods such as radiography.

It is intended during the next seven years to compile new monographs on methods of analysis and the analytical chemistry of individual elements.

One of the most important problems is to improve the organization of scientific-research work, in particular to establish a more rational distribution of the large centers of analytical chemistry. It is necessary to set up a center beyond the Urals so as to ensure that the ever-increasing contigent of analytical chemists in Siberia and the Far East have access to scientific consultation. Coordination of scientific-research work, which should be improved, should be realized not only by convening conferences, but also of scientific conferences, and, to a significant extent, by the active participation of journals on analytical chemistry.

The solution of the new problems set before our analytical chemistry by life, and also the general reorganization of the system of national education in the country, demand improvements in the calibre of analytical chemists. Of fundamental importance in this connection is the acquisition of more profound theoretical knowledge, in the first instance of a physicochemical nature, as well as practical mastery of the most modern, methods of analysis, particularly instrumental methods.

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COLOR REACTIONS OF URANIUM AND THORIUM WITH o'-ARSONO-o'-HYDROXY-AZO-COMPOUNDS*

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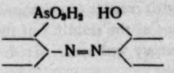
It has been found previously that some compounds containing the atomic group 1 are valuable analytical reagents for the photometric determination of Th, U, total rare earths, Zr, Be and some other elements [1-2]. At present, two reagents found more than 15 years ago, namely thoron and arsenazo (uranon), are finding wide application. They have been recommended for the photometric determination and detection by color reactions of thorium [2-18], uranium [19], the rare earths [20], zirconium [21-22], beryllium [23-25], vanadium [26], lithium [27-29], aluminum [30], and other elements. Thoron is issued as a reagent by foreign firms [31]. Arsenazo—under the name "neotron" — has been recommended by Japanese research workers [32]** for the determination of thorium.

The value of the reagents arsenazo and thoron led the author to study the closest analogs of these reagents. The present article is devoted to some results on the analytical reagents of some of these analogs. The work was carried out in 1942. Some of these analogs, particularly those containing two of these groups in the same molecule,*** proved to be more valuable reagents than arsenazo and thoron.

In accordance with general rules [36, 37] uranium and thorium can give color reactions with many azo-, azomethine, and other colored compounds containing the following atomic groups:



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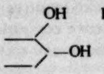

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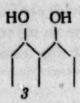

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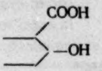

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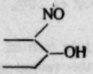

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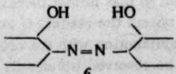

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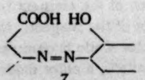

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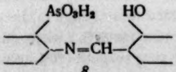

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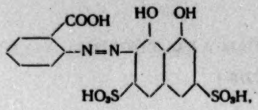
*A paper read on the 12th of March 1957 at a session of the Science Council of the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry Acad. Sci. USSR; the paper was devoted to the memory of V. I. Vernadskii.

**The Japanese authors' paper contains no reference to the article of the present author. Presumably, the work of the author [1, 2] was not known to them, although references to this work had been published in Chem. Abstracts and Chem. Zentralblatt, and had been dealt with in detail in F. Welcher's textbook "Organic Analytical Reagents," Vol. IV, pp. 474-75.

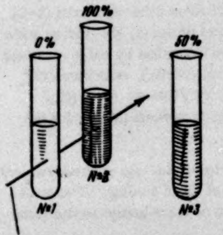
***There have been published references in recent years to the fact that duplication of the same characteristic atomic group in the reagent molecule leads to reagents which give more stable complexes than reagents containing only one such group. Many examples can be quoted to confirm this assertion. This fact is particularly clearly shown in the case of the analogs of 8-hydroxyquinoline [33] and various azo-compounds [34].

of which 2, 3, 4, and 5 may enter into the composition of azo-compounds, di-, and triphenylmethane dyes, hydroxyanthraquinone or indophenols. Of the large number of such possible reagents, those containing group 1 are particularly interesting from the point of view of selectivity, stability of their complexes, and some other characteristics. The reagent arsenazo which contains group 1, forms complexes with U and Th which are more stable than those formed by these metals with its analog which has the following structure



this contains the carboxyl group COOH and not the group AsO_3H_2.

Sensitivity of color reactions and stability of the complexes. In Table 1 are given the formulas and rational names of the compounds tested, while Table 2 gives the colors of their solutions, and the colors which develop in the presence of excess thorium. It is evident that compounds in whose molecule group 1 is duplicated, i.e., containing two of the group 1 moieties, do not differ essentially in all cases in color from compounds containing this group only once. But, this duplication of the same group within the molecule essentially increases the stability of the complexes formed by the compound. This means that the complexes of these reagents can be formed under less favorable conditions: at higher acidities, or in the presence of large amounts of phosphates, sulfates, fluorides, and other masking agents. For these reasons reagents with a duplicated group are more valuable than their "monomeric" analogs. Of particular interest are the reagents "thoron II" (VII) and "arsenazo II" (VIII). Examples which illustrate the effect of this duplication of group 1 in the reagent molecule on the stability of the complexes, and the reaction sensitivity connected with this, are given in Table 3. The high sensitivity of the reaction in weakly-acid media with the azo derivatives of chromotropic acid (arsenazo, arsenazo II, X) as compared with that of the corresponding azo derivatives of R-acid (thoron, thoron II, IX) can be explained by the greater contrast of the color changes. But, on the other hand, substituted chromotropic acids are more sensitive with respect to enhanced acidity. In order to make an objective comparison of the stability of the complexes of uranium and thorium formed by the compounds being tested, a new technique was used. We shall give a brief description of this technique.*



Shade characteristic of binding to the extent of 50%.

Preparing a shade corresponding to binding of the reagent as a complex to the extent of 50%.

At the test pH, the necessary concentration of the element is chosen so that further increases in this concentration will not lead to a change in the color of the reagent. In this system the reagent is almost completely complexed ("100% color shade"). When this color shade is observed in conjunction with the color of the same concentration of the pure reagent ("0% color shade"), a color shade will be observed which will correspond to the case where the reagent has reacted to the extent of 50% (see Fig. No. 1 and No. 2). It is not difficult to obtain the 50% shade even in one solution, by selecting the concentration of element needed for this, and then taking, for convenience in comparison, double the concentration of the reagent (see Fig. No. 3).

At a constant pH and constant reagent concentration, a definite concentration of free ions of the element corresponds to each color shade. When, for example, an additional amount of element is added to a system with a 50% color shade, and, at the same time, an amount of a chosen masking agent for complexing the element is added so that the shade still remains 50%, then at constant volume, under these conditions, the additional amount of element will be completely masked. This follows from the fact that the equilibrium concentration of the free ions of the element for the system element—reagent and element—masking material is the same, while the equilibrium concentration of free ions of the element required is already created in the

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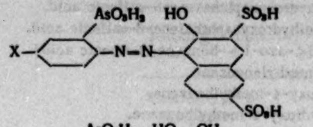
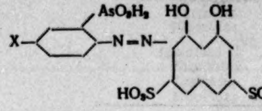
*This technique will be described in detail in subsequent articles.

TABLE 1

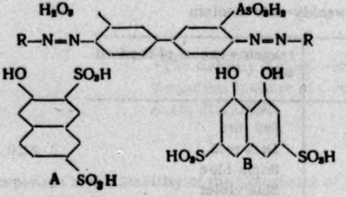
Formulas of the Compounds Tested



X = H — I (thoron)
O_2N — II (nitrothoron)
NH_2 — III (aminothoron)

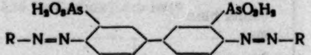


H — IV (arsenazo)
O_2N — V (nitroarsenazo)
H_2N — VI (aminoarsenazo)

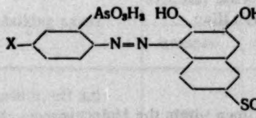


R = A VII (thoron II)

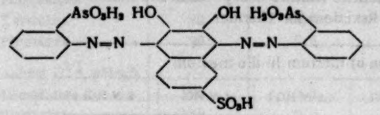
B VIII (arsenazo II)



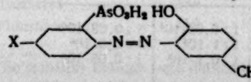
R = A IX
B X



X = H — XI
O_2N— XII
H_2N— XIII



XIV



X = H — XV
O_2N — XVI
H_2N— X VII

I. Benzene-2-arsonic acid-<1-azo-1>-2-hydroxynaphthalene-3,6-disulfonic acid.
II. 4-Nitrobenzene-2-arsonic acid-<1-azo-1>-2-hydroxynaphthalene-3,6-disulfonic acid.
III. 4-Aminobenzene-2-arsonic acid-<1-azo-1>-2-hydroxynaphthalene-3,6-disulfonic acid.
IV. Benzene-2-arsonic acid-<1-azo-7>-1,8-dihydroxynaphthalene-3,6-disulfonic acid.
V. 4-Nitrobenzene-2-arsonic acid-<1-azo-7>-1,8-dihydroxynaphthalene-3,6-disulfonic acid.
VI. 4-Aminobenzene-2-arsonic acid-<1-azo-7>-1,8-dihydroxynaphthalene-3,6disulfonic acid.
VII. Diphenyl-4,4'-diarsonic acid-3,3'-bis [<-azo-1>-2-hydroxynaphthalene-3,6-disulfonic acid].
VIII. Diphenyl-4,4'-diarsonic acid-3,3'-bis [<-azo-7>-1,8-dihydroxynaphthalene-3,6-disulfonic acid].
IX. Diphenyl-3,3'-diarsonic acid-4,4'-bis [<-azo-1>-2-hydroxynaphthalene-3,6-disulfonic acid].

X. Diphenyl-3,3'-diarsonic acid-4,4'-bis [<-azo-7>-1,8-dihydroxynaphthalene-3,6-disulfonic acid].

XI. Benzene-2-arsonic acid-<-azo-1>-2,3-dihydroxynaphthalene-6-sulfonic acid.

XII. 4-Nitrobenzene-2-arsonic acid-<1-azo-1>-2,3-dihydroxynaphthalene-6-sulfonic acid.

XIII. 4-Aminobenzene-2-arsonic acid-<1-azo-1>-2,3-dihydroxynaphthalene-6-sulfonic acid.

XIV. 2,3-Dihydroxynaphthalene-6-sulfonic acid-1,4-bis[<-azo-1>-benzene-2-arsonic acid].

XV. Benzene-2-arsonic acid-<1-azo-6>-1-hydroxy-4-methyl-benzene.

XVI. 4-Nitrobenzene-2-arsonic acid-<-azo-6>-1-hydroxy-4-methylbenzene.

XVII. 4-Aminobenzene-2-arsonic acid-<-azo-6>-1-hydroxy-4-methylbenzene.

TABLE 2

Color Reactions of Thorium

Compound	Color in weakly-acid medium	
	reagent alone	reagent + excess of thorium salt
Thoron (I)	Yellow	Red rose
Thoron II (VII)	Orange yellow	Dark rose
(IX)	Bluish raspberry	Bright blue
Arsenazo (IV)	Orange red	Blue violet
Arsenazo II (VIII)	Orange red	Violet blue
(X)	Red violet	Blue
(XI)	Orange yellow	Brownish rose
(XIV)	Orange rose	Brown lilac

TABLE 3

Effect of the Duplication of the Same Characteristic Atomic Group within the Molecule of the Reagent on the Sensitivity of the Color Reactions for Thorium

Reagent	Limiting dilution of thorium in the medium				
	acetic	0,1 N HCl	0,5 N HCl	1 N HCl	2 N HCl
Thoron	$1:3\cdot10^6$	$1:1,5\cdot10^6$	$1:0,2\cdot10^6$	$1:0,08\cdot10^6$	$1:0,03\cdot10^6$
Thoron II	$1:3\cdot10^6$	$1:1,5\cdot10^6$	$1:1,2\cdot10^6$	$1:1\cdot10^6$	$1:0,5\cdot10^6$
IX (at. group dupl.)	$1:5\cdot10^6$	$1:2\cdot10^6$	$1:0,3\cdot10^6$	$1:0,1\cdot10^6$	$1:0,05\cdot10^6$
Arsenazo	$1:5\cdot10^6$	$1:0,75\cdot10^6$			
Arsenazo II	$1:8\cdot10^6$	$1:1,5\cdot10^6$			
X (at. group dupl.)	$1:6\cdot10^6$	$1:1,5\cdot10^6$			

solution on reproducing the 50% shade. The molar ratio of the masking agent introduced to the amount of element added, expressed in moles, characterizes the stability of the complex formed by the element and the test reagent. We shall call this value the "stability index of the complex." By comparing, in this way, the results for various reagents, it is possible to get accurate, fully objective stability characteristics of the complexes formed by these reagents. The higher the stability index, the more stable the complex formed with the element. Table 4 contains stability indices for the complexes of uranium and thorium formed by reagents containing one (thoron, arsenazo), and two (thoron II, arsenazo II) of these atomic groups 1. Table 5 contains similar data for arsenazo and its analog similar in structure; arsenazo, however, contains group 1, while its analog contains group 7.

TABLE 4

Comparative Stability of Complexes Formed by the "Single" and "Double" Reagents*

Masking complexing agent	Indices of the stability of the complex			
	arsenazo	arsenazo II	thoron	thoron II
Thorium, pH 3				
Phosphates	200	400	15	1000
Tartrates	70	300	100	800
Fluorides	20	30	7	~80
Uranium U^{VI}, pH 4.5				
Phosphates	125	250	~2	~3
Tartrates	160	320	~3	~50
Fluorides	110	180	~10	~200

---

*The stability indices were determined by S. B. Savvin (The V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR).

TABLE 5

Comparison of the Stability of the Complexes of Arsenazo and Its Carboxy Analog*

Masking agent	Stability index of the complex	
	arsenazo	carboxyl analog
Thorium, pH 3.0		
Phosphates	200	1.4
Tartrates	70	1.6
Fluorides	20	2.8
Uranium U^{VI}, pH 4.5		
Phosphates	120	0.8
Tartrates	160	0.5
Fluorides	110	2

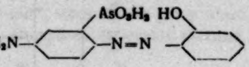
---

*The stability indices were determined by S. B. Savvin (The V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR).

Contrast of the Color Reactions

In Table 6 are given the colors which develop during the reactions with some of the reagents under discussion.

With respect to the contrast of color reactions, reagents containing the amino group, i.e., those containing the following atomic group



are outstanding. Reagents of this type give very contrasting color reactions and deep colors with thorium. Solutions of these reagents themselves differ very little from solutions of their analogs not containing the NH_2 group (Table 7).

The reasons for the high contrast of the color reactions of reagents containing the NH_2 group, has been discussed in general terms previously [37]. Here, as the result of the formation of a complex in the reagent molecule, there arises a strongly pronounced dipole. An "electric contrast" — in Witsinger's [38] terminology—develops between the different ends of the molecule of the complex, and this circumstance leads to a sharp change in color of the reagent when it is converted into the complex.

In order to illustrate this influence on the color, we may mention an example given in the article on the chromophoric action of the elements [39]. Diazotized amino-hydroxy-azo compounds containing these groups in different nuclei, in the ortho or in the para positions to the azo group, for example

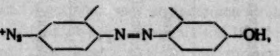


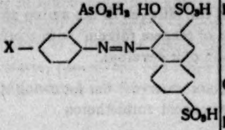
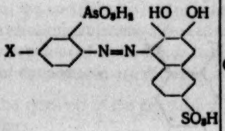
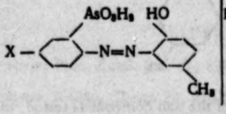
TABLE 6

Color Reactions of Certain Elements at pH 2-4, Except for U^{VI} and Rare-Earths (pH 5-6)

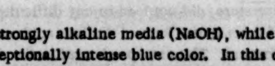
Reagent	Color									
	reagent alone	Th and U^{IV}	U^{VI}	total rare earths	Ti	Zr	Sn^{IV}, β-compound	Sb^{III}	Nb^{V}	Fe^{III}
Thoron	Yellow	Rose	Red	Red	Orange	Red-orange	Orange	Orange-red	Orange	Brown
Thoron II	Orange-red	Rose	Rose	Rose	Red-orange	Red-orange	Orange	Orange-red	Red-orange	Brown-red
IX	Rose	Blue	Blue	Blue-violet	Rose	Rose	Rose	Pale violet	Rose	Brown-red
Arsenazo	Orange-red	Blue-violet	Blue	Violet	Violet	Violet	Orange-red	Orange-red	Violet	Brown-violet
Nitrothoron	Yellow-orange	Rose	Red	Red	Orange	Orange	Orange	Pale rose	Yellow orange	Brown
Amino-thoron	Brown-rose	Blue-violet	Brown-violet	Red-violet	Brown-red	Brown-rose	Brown-yellow	Rose-brown	Brown	Brown-yellow
IX	Orange-yellow	Red	Red	Red	Red	Red	Orange	Rose	Rose	Brown-violet

TABLE 7

Effect of the H_2N Group in Reagent Molecules on the Contrast of Color Reactions with Thorium

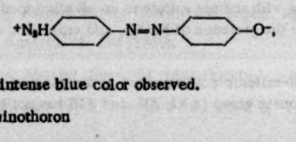
№		X	Color	
			reagent alone	reagent + Th
III		H_2N—	Brownish-rose	Blue-violet
I		H—	Yellow	Rose
II		O_2N—	Yellow-orange	Red-rose
XIII		H_2N—	Orange-yellow	Red-violet
XI		H—	Orange-yellow	Red
XII		O_2N—	Orange-yellow	Orange-red
				Greenish-yellow
XVII		H_2N—	Yellow	Yellow
XV		H—	Yellow	Yellow
XVI		O_2N—	Yellow	

possess a yellow color in acid or in strongly alkaline media (NaOH), while in weakly alkaline media (ammonia, sodium carbonate) they have an exceptionally intense blue color. In this case, in the acid medium or in the strongly alkaline medium there is no strongly developed "electric contrast", since the OH group is not ionized in acid media, while in strongly alkaline media the diazonium cation disappears. In weakly alkaline media, however, the ionic state of the OH group and the diazonium cation



coexist and this fact leads to the intense blue color observed.

In the case of the reagent aminothoron



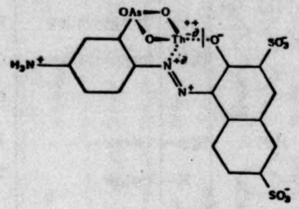
we have a molecule in which both the NH_2 and OH groups are in an ionic state, and we get the intense color associated with this state, whatever the pH. In the cyclic salts formed by aminothoron, as a result of innermolecular dissociation of these salts [36] the oxygen of the phenolic group may be in an ionic state even in acid media. When the acidity is sufficient for the NH_2 group to change into a salt, then this group also will be in an ionic state. Since thorium forms a complex with aminothoron in strongly acid media, while the rare earths, particularly La, form complexes in very weak acid where the NH_2 hardly changes at all into the ionic state, it is readily understood why a more intense color is given with thorium than with lanthanum.

Aminothoron gives the following colors:

Reagent alone	pH 3—6	Brownish-rose
Thorium	3.0	Blue-violet
Uranium (VI)	4.2	Brownish-violet
Lanthanum	6.0	Brownish-raspberry

Aminothoron only forms brownish-rose and brownish-reddish colors with zirconium and titanium, respectively. It would be thought that with these elements, as with thorium, there should develop intense violet colors, since the reactions take place in a strongly acid medium. This, however, is not the case because zirconium and titanium only weakly favor the change over into the ionic state of the nitrogen of the amino group, which also deepens the color. The same phenomenon is observed in the case of reagent thoron: with thorium a rose color develops, while with zirconium and titanium only an orange-red color develops.

Taking into account chemical considerations and the color observed, the following structure can be assigned to the violet stage of the complex of thorium with the reagent aminothoron



Synthesis of the compounds tested. Synthesis of most of the azo compounds tested, many of which have not hitherto been described in the literature, did not lead to any difficulties and was carried out by the usual azo coupling method. Almost all of them in the form of the free acids or their salts can be readily crystallized, so that their purification is straightforward. The compounds used as the diazotized component were the following compounds which have been described in the literature: 2-aminophenyl-arsonic acid [40], 3,3'-diaminodiphenyl-4,4'-diarsonic acid [41], and 5-nitro-2-aminophenylarsonic acid [42].

Compounds containing the NH_2 group were obtained from the corresponding nitro compounds by reduction of the latter by gentle heating with sodium sulfide in an alkaline medium, followed by precipitation of excess sulfide with copper salts (in the presence of NaOH), and separation of the end-product by acidification or salting out (aminothoron).

2,3-Dihydroxynaphthalene-6-sulfonic acid was used as the azo component for the compounds XI, XII, and XIV. The position of the sulfonate group in XI, XII, and XIII has not been established; it is possible that it occupies position 7, not 6.

Benzidene-3,3'-diarsonic acid, which apparently has not yet been described in the literature, was used for synthesizing IX and X. We did not isolate it in a pure form. The reaction product obtained from o-nitrophenyl arsonic acid was used directly without purification for diazotization and coupling; it was prepared in a similar manner to that used for the preparation benzidene-3,3'-dicarboxylic acid by reduction to the hydrazo compound, by the action of zinc dust and NaOH, with subsequent regrouping in the presence of concentrated hydrochloric acid. In view of the ease with which it could be oxidized, the pale-yellowish alkaline solution of the hydrazo compound was filtered from the zinc sludge directly into cold concentrated hydrochloric acid. The monoazo compound (reduction of o-nitrophenylarsonic acid to o-aminophenylarsonic acid) predominated in the products obtained by azo coupling.

Diazo compounds IX and X were separated and purified chromatographically on Al_2O_3. Dilute 0.5-1% acetic acid completely elutes the monoazo compound, while it does not elute the diazo compound. After elution of the monoazo compound, the diazo compound was eluted with a solution of $NaHCO_3$. The yield of final IX and X, calculated on the basis of o-nitrophenylarsonic acid was very small.

SUMMARY

Colored organic reagents which give color reactions with uranium and thorium may contain various characteristic atomic groups. The most interesting reagents are those which contain group 1; the well-known reagents thoron and arsenazo belong to this category. The color reactions of 15 other compounds containing this characteristic atomic group have been studied.

New reagents, thoron II (diphenyl-4,4'-diarsonic acid-3,3'-bis[<-azo>-2-hydroxynaphthalene-3,6-disulfonic acid]), and arsenazo II (diphenyl-4,4'diarsonic acid-3,3'-bis[<-azo-7>-1,8-dihydroxynaphthalene-3,6-disulfonic acid]) in which group 1 is duplicated, are described. The molecules of these new reagents are doubled molecules of thoron and arsenazo, respectively. Arsenazo II and thoron II give more stable complexes than arsenazo and thoron, as a result of which colors develop in more acid solutions and in the presence of larger amounts of sulfates, phosphates, and other masking agents, than when arsenazo and thoron are used. The shade of the colors which are formed by arsenazo II and thoron II differ little from those given by arsenazo and thoron.

With respect to the contrast of its color reaction, the reagent aminothoron (4-aminobenzene-2-arsonic acid-<-azo-1>-2-hydroxynaphthalene-3,6-disulfonic acid) is outstanding; it gives a violet color with thorium in acid media. The solutions of aminothoron itself are yellow brown in color. The reasons for the contrast of the color reactions of aminothoron are discussed.

Schemes for the synthesis of the compounds tested are given; most of them have not hitherto been described in the literature.

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SOME CHARACTERISTICS OF SELENOYL-2-ACETONE AND BENZOYLACETONE

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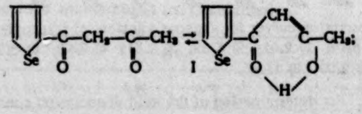
In studying complex formation processes by means of the distribution method (extraction), it is necessary to carry out a preliminary determination of the constants of acid dissociation of the reagents used, and also the partition constants of the undissociated molecules of these reagents in the systems chosen, at different concentrations of reagent in the organic solvent layer [1, 2]. In the work described here, these characteristics were determined for selenoyl-2-acetone which has been synthesized for the first time (I) and benzoylacetone which has been described previously (II).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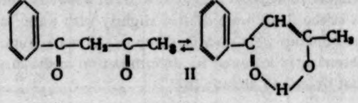
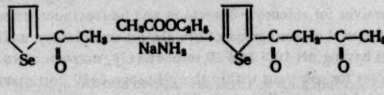

II

EXPERIMENTAL

Reagents used. Selenoyl-2-acetone was synthesized for the first time by N. N. Mezentseva in the laboratory of Yu. K. Yur'ev according to the following scheme:



To sodium amide obtained from 8.6 g of sodium [13] and dissolved in 300 ml of absolute ether contained in a three-necked flask fitted with a stirrer, condenser, and dropping funnel, was added, at 20° with stirring, a solution of 30 g (0.17 g · mole) of methyl-(selenoyl-2)-ketone in 25 ml of absolute ether; this was followed by a solution of 40 g (0.45 g · mole) of absolute ethyl acetate in 40 ml of absolute ether. The reaction mixture was stirred for 15 minutes at 20°, and for 3 hours while heating on a water bath. After cooling, the reaction mass was decomposed with a mixture of ice (about 400 g) and 90 ml of concentrated hydrochloric acid and the resultant mixture extracted with ether. The combined ether extracts were dried with anhydrous magnesium sulfate. After distilling off the ether, the residue was distilled under vacuum. 26 g of product was obtained (71%); the boiling point was 146-146.5° at 7 mm (a viscous oil with a straw-yellow color which crystallized in the receiver); m.p. 33-33.5° (from alcohol). Analysis in % C 44.81, 44.77; H 3.87, 3.80; Calculated in %: C 44.67; H 3.75. The preparation was carefully purified and stored until its weight was almost constant.

The benzoylacetone which was synthesized [4] was subjected to repeated crystallization from ethanol until white crystals with a m. p. of 58.5-59° were obtained. The absorption spectrum of the reagent thus prepared agreed with that published in the literature [5]. The benzoylacetone was stored in a desiccator until its weight was almost constant. Preparation of the NaOH and $NaClO_4$ solutions used in the course of the work, as well as purification of the solvents used, were the same as described previously [6].

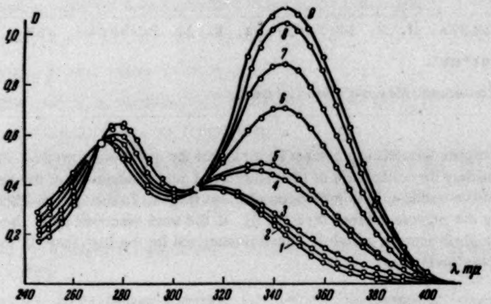


Fig. 1. Absorption curves for aqueous solutions of selenoyl-2-acetone at various pH's: 1) 2.01; 2) 5.32; 3) 7.51; 4) 7.92; 5) 8.20; 6) 8.60; 7) 9.12; 8) 9.90; 9) 11.15.

Experimental procedure. For determination of the acid dissociation constants of the reagents, known equal volumes of an aqueous solution of the test reagent (the reagent solution was prepared by dissolving a small amount of the solid reagent in aqueous $HClO_4$ at a pH of about 1) were introduced into a series of 50 ml flasks; the reagent solutions in the flasks were diluted slightly with water and the calculated amounts of NaOH and 0.5 N $NaClO_4$ added, the volumes were then made up to the mark (ionic strength of the final solution was $\mu = 0.1$). The procedure subsequently followed for determination of the dissociation constants and the partition constants was the same as that described already [6].

Determination of the acid dissociation constant of selenoyl-2-acetone and benzoylacetone was carried out photometrically using the method of "isobestic points" [7], which has been successfully used for studying the reagents themselves [8-10] as well as complexes formed by reagents with metals [11]. On the absorption curves of aqueous solutions of selenoyl-2- and benzoylacetone, having different pH values, there is observed a definite shift in the absorption maximum; this shift is determined by the dissociation of the reagent, and by differences in the absorption of its dissociated and undissociated forms (Figs. 1 and 2).* It was established beforehand that the absorption curves for selenoyl-2-acetone and benzoylacetone solutions having a pH of < 2.5 and ≤ 2.1, respectively, correspond to absorption of the almost completely undissociated forms, while the absorption curves for solutions having pH 10.9 and 10, respectively, correspond to absorption of the almost completely dissociated forms (curves for solutions within the pH range 5-10 correspond to absorption by mixtures of the dissociated and undissociated forms of the reagents). At a constant total concentration of the reagent in aqueous solution, the value of the acid dissociation constant is calculated according to the following equation

$$K_{\text{dissoc.}} = \frac{(A_{\text{mixture}} - A_{\text{undissoc.}})}{(A_{\text{dissoc.}} - A_{\text{mixture}})} \cdot (H^+), \qquad (1)$$

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* In the middle region of Fig. 1, the numeration of the curves is the reverse of that for the right-hand side. Some of the curves coincide with each other between the first and second "isobestic" points.

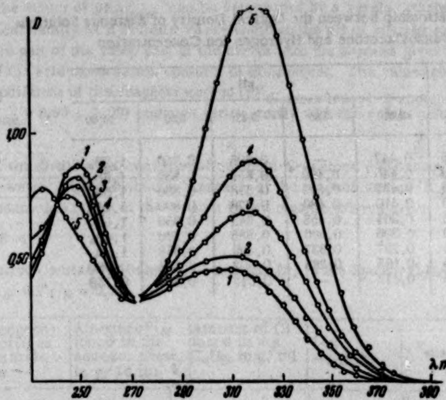

Fig. 2. Absorption curves for aqueous solutions of benzoylacetone at various pH values: 1) 2.06; 2) 7.85; 3) 8.42; 4) 8.90; 5) 10.90.

TABLE 1

Relationship between the Optical Density of Aqueous Solutions of Selenoyl-2-acetone and Hydrogen Ion Concentration

λ mμ	pH					
	2,01	7.92	8,20	8,60	9,12	11,15
330	0,317	0,455	0,473	0,620	0,760	0,920
335	0,280	0,454	0,480	0,665	0,820	1,010
340	0,243	0,443	0,473	0,700	0,870	1,080
345	0,201	0,422	0,456	0,705	0,880	1,120
350	0,160	0,385	0,422	0,675	0,860	1,090
355	0,122	0,345	0,376	0,628	0,800	1,030
360	0,087	0,295	0,327	0,553	0,705	0,912
365	0,063	0,244	0,273	0,465	0,600	0,780
370	0,046	0,196	0,218	0,380	0,482	0,630

Note, Only curves 4, 5, 6, and 7 (Fig. 1) were used for calculation. Curves 2, 3, and 8 were not used since the small difference in optical densities obtained thereby, may lead to appreciable errors in the value of $K_{dissoc.}$.

where $A_{undissoc.}$, $A_{dissoc.}$, and $A_{mixture}$ are the optical densities of solutions containing the undissociated, dissociated, and mixtures of dissociated and undissociated forms of the reagent, respectively, for a given wavelength and (H^+) is the hydrogen ion concentration of the solution containing both forms of the reagent. The values of the optical density chosen for calculation are given in Tables 1 and 2 for selenoyl-2-acetone and benzoylacetone, respectively. The calculated values for the reciprocal logarithm of the dissociation constant ($pK_{dissoc.}$) of selenoyl-2-acetone and benzoylacetone are: $pK_{dissoc.} = 8.55 \pm 0.08$ (mean of 36 calculated values) and $pK_{dissoc.} = 8.96 \pm 0.09$ (mean of 27 calculated values), respectively.

TABLE 2

Relationship between the Optical Density of Aqueous Solutions of Benzoylacetone and Hydrogen Ion Concentration

λ mμ	pH				
	2,06	7,85	8,42	8,90	10,90
305	0,442	—	0,605	0,750	1,20$_0$
310	0,446	0,490	0,651	0,830	1,38$_0$
315	0,436	0,510	0,678	0,880	1,50$_0$
320	0,410	0,480	0,678	0,890	1,51$_0$
325	0,364	0,458	0,642	0,850	1,50$_0$
330	0,306	0,406	0,585	0,770	1,40$_0$
335	0,237	0,337	0,499	0,658	1,20$_0$
340	0,165	0,265	0,402	0,528	0,980
345	0,112	—	0,310	0,404	0,748

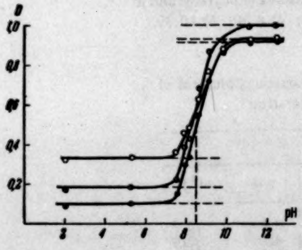

Fig. 3. Relation between the optical density of solutions of selenoyl-2-acetone and the pH at various wave lengths ○) 330 mμ; ☐) 350 mμ; Δ) 360 mμ.

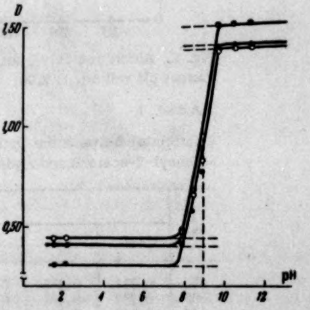

Fig. 4. Relation between the optical density of solutions of benzoylacetone and the pH at various wave lengths ○) 310 mμ; ☐) 320 mμ; Δ) 330 mμ.

TABLE 3

Distribution Constant (I) of Selenoyl-2-acetone in the System $CHCl_3-H_2O$ (t = 25 ± 0.1°; μ = 0.1)

Initial concentration in $CHCl_3$, in moles/liter	Amount of (I) found in the aqueous phase in g/15 ml	Amount of (I) found in the $CHCl_3$ phase, in g/15 ml	Log $K_{distrib.}$	$K_{distrib.}$
$1,29 \cdot 10^{-1}$	$4,95 \cdot 10^{-4}$	$41,54 \cdot 10^{-2}$	2,924	839
$6,50 \cdot 10^{-2}$	$2,49 \cdot 10^{-4}$	$20,77 \cdot 10^{-2}$	2,921	834
$5,00 \cdot 10^{-2}$	$1,98 \cdot 10^{-4}$	$16,12 \cdot 10^{-2}$	2,911	815
$3,90 \cdot 10^{-2}$	$1,44 \cdot 10^{-4}$	$12,46 \cdot 10^{-2}$	2,937	851
$2,50 \cdot 10^{-2}$	$0,96 \cdot 10^{-4}$	$80,60 \cdot 10^{-3}$	2,924	839
$1,00 \cdot 10^{-2}$	$0,39 \cdot 10^{-4}$	$32,25 \cdot 10^{-3}$	2,917	826
$5,00 \cdot 10^{-3}$	$0,18 \cdot 10^{-4}$	$16,12 \cdot 10^{-3}$	2,952	895

It is known that the values of $pK_{dissoc.}$ can be determined by a purely graphical method from the curves relating the optical density at a definite wave-length to the pH of aqueous solutions. The perpendicular dropped from the middle part of the steep part of the curves onto the abscissa gives the numerical value of the reciprocal logarithm of the acid dissociation constant of the reagent. The values obtained in this way (Figs. 3 and 4) for the acid dissociations of the reagents studied ($pK_{dissoc.\,selenoyl-2-acetone} = 8.60 \pm 0.07$ and $pK_{dissoc.\,benzoylacetone} = 8.90 \pm 0.09$) coincide satisfactorily with the values calculated from the absorption curves.

Determination of the distribution constants of selenoyl-2-acetone and benzoylacetone in systems of chloroform or benzene-water. The distribution constants of the reagent studied ($K_{distrib.}$)* must be determined over a fairly wide concentration range of the reagent in the organic solvent layer.

TABLE 4

Distribution Constant of Selenoyl-2-acetone (I) in the System C_6H_6—H_2O
($t = 25 \pm 0.1°$; $\mu = 0.1$)

Initial concentration of (I) in C_6H_6, in mole per liter	Amount of (I) found in the aqueous phase, in g/15 ml	Amount of (I) found in the C_6H_6, in g/ml	Log $K_{distrib.}$	$K_{distrib.}$
$8{,}74\cdot10^{-2}$	$2{,}73\cdot10^{-4}$	$28{,}17\cdot10^{-2}$	2,998	995
$5.83\cdot10^{-2}$	$1{,}83\cdot10^{-4}$	$18{,}78\cdot10^{-2}$	3,011	10.6
$4{,}37\cdot10^{-2}$	$1{,}38\cdot10^{-4}$	$14{,}09\cdot10^{-2}$	3,009	1021
$2{,}91\cdot10^{-2}$	$0{,}90\cdot10^{-4}$	$93{,}91\cdot10^{-3}$	3,012	1028
$1{,}75\cdot10^{-2}$	$0{,}57\cdot10^{-4}$	$56{,}34\cdot10^{-3}$	2,995	988
$1{,}16\cdot10^{-2}$	$0{,}39\cdot10^{-4}$	$37{,}56\cdot10^{-3}$	2,984	964
$8{,}74\cdot10^{-3}$	$0{,}26\cdot10^{-4}$	$28{,}17\cdot10^{-3}$	3,018	1042

TABLE 5

Distribution Constant of Benzoylacetone (II) in the System $CHCl_3$—H_2O
($t = 25 \pm 0.1°$; $\mu = 0.1$)

Initial concentration of (II) in $CHCl_3$, in mole per liter	Amount of (II) found in the aqueous phase, in g/15 ml	Amount of (II) found in the $CHCl_3$ phase, in g/15 ml	Log $K_{distrib.}$	$K_{distrib.}$
$1{,}50\cdot10^{-1}$	$1{,}26\cdot10^{-4}$	$36{,}48\cdot10^{-2}$	3,462	2897
$1{,}30\cdot10^{-1}$	$1{,}17\cdot10^{-4}$	$31{,}61\cdot10^{-2}$	3,432	2704
$1{,}20\cdot10^{-1}$	$1{,}02\cdot10^{-4}$	$29{,}18\cdot10^{-2}$	3,457	2864
$1{,}00\cdot10^{-1}$	$0{,}87\cdot10^{-4}$	$24{,}32\cdot10^{-2}$	3,447	2799
$5{,}00\cdot10^{-2}$	$0{,}45\cdot10^{-4}$	$12{,}16\cdot10^{-2}$	3,432	2704
$3{,}00\cdot10^{-2}$	$0{,}27\cdot10^{-4}$	$72{,}95\cdot10^{-3}$	3,432	2704
$2{,}00\cdot10^{-2}$	$0{,}18\cdot10^{-4}$	$48{,}64{,}10^{-3}$	3,432	2704
$1{,}50\cdot10^{-2}$	$0{,}15\cdot10^{-4}$	$36{,}46\cdot10^{-3}$	3,386	2432

We studied the distribution of undissociated molecules of selenoyl-2-acetone and benzoylactone in the systems $CHCl_3$—H_2O and C_6H_6—H_2O at an ionic strength of the latter of $\mu = 1$, and at a temperature of 25 ± ± 0.1°, for the original concentrations of reagents in the organic solvent indicated in Tables 3, 4, 5, and 6. The values obtained for the distribution constant of selenoyl-2-acetone are given in Tables 3 and 4; while analogous results are given for benzoylacetone in Tables 5 and 6. The nature of the changes in $K_{distrib.}$ in the studied concentration range of the reagents is evident from Figs. 5 and 6 (values for log $K_{distrib.}$** are given.

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*$K_{distrib.} = \frac{C_{org.}}{C_{water}}$, where C_{org} and C_{water} are the equilibrium concentrations of the reagent in the organic and aqueous-phases, respectively.

**Each value for $K_{distrib.}$ given in Tables 3-6 is the mean of two-three replicate determinations.

TABLE 6

Distribution Constant of Benzoylacetone (II) in the System $C_6H_6 - H_2O$ (t = = 25 ± 0.1°; μ = 0.1)

Initial concentration of (II) in C_6H_6, in mole per liter	Amount of (II) found in the aqueous phase, in g/15 ml	Amount of (II) found in the C_6H_6 phase, in g/15 ml	Log $K_{distrib.}$	$K_{distrib.}$
$1{,}50 \cdot 10^{-1}$	$2{,}64 \cdot 10^{-4}$	$36{,}45 \cdot 10^{-2}$	3,140	1380
$1{,}30 \cdot 10^{-1}$	$2{,}28 \cdot 10^{-4}$	$31{,}60 \cdot 10^{-2}$	3,142	1387
$1{,}20 \cdot 10^{-1}$	$2{,}04 \cdot 10^{-4}$	$29{,}17 \cdot 10^{-2}$	3,155	1429
$1{,}00 \cdot 10^{-1}$	$1{,}71 \cdot 10^{-4}$	$24{,}31 \cdot 10^{-2}$	3,153	1422
$5{,}00 \cdot 10^{-2}$	$0{,}87 \cdot 10^{-4}$	$12{,}15 \cdot 10^{-2}$	3,145	1396
$3{,}00 \cdot 10^{-2}$	$0{,}54 \cdot 10^{-4}$	$72{,}90 \cdot 10^{-3}$	3,130	1349
$2{,}00 \cdot 10^{-2}$	$0{,}33 \cdot 10^{-4}$	$48{,}62 \cdot 10^{-3}$	3,168	1472
$1{,}50 \cdot 10^{-2}$	$0{,}27 \cdot 10^{-4}$	$36{,}45 \cdot 10^{-3}$	3,130	1349

For calculating the mean value of $K_{distrib.}$ (Tables 3-6), results which did not differ from each other by more than 6% were used. The values found for the distribution constant of selenoyl-2-acetone were as follows: 1) for the system $CHCl_3-H_2O$, $K_{distrib.}$ = 839 ± 9 (log $K_{distrib.}$ = 2.922 ± 0.006); 2) for the system C_6H_6, $K_{distrib.}$ = = 1009 ± 23 (log $K_{distrib.}$ = 3.004 ± 0.010).

The values found for the distribution constant of benzoylacetone were as follows: 1) for the system $CHCl_3-H_2O$, $K_{distrib.}$ = 2746 ± 60 (log $K_{distrib.}$ = 3.439 ± 0.009); 2) for the system $C_6H_6-H_2O$, $K_{distrib.}$ = = 1398± 32 (log $K_{distrib.}$ = 3.145 ± 0.010).

DISCUSSION OF RESULTS

The fact that there are two fairly clearly defined isobestic points on the absorption curves for aqueous solutions of both selenoyl-2-acetone and benzoyl acetone, indicates the presence of two absorption centers in the solution. The predominance of one of the forms of the reagent, under certain conditions, is confirmed by the almost complete coincidence of the absorption curves obtained for groups of solutions having a pH less than 2 and greater than 10, and also by the fact that the absorption exhibited by the solutions conforms to the Beer Law at various wave lengths. (this fact was verified for the group of solutions with pH > 10).

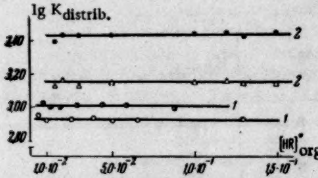

Fig. 5. Relation between the distribution constant of selenoyl-2-acetone (I) and benzoylacetone (II), and the concentration of reagent in the organic solvent (1– ○ – $CHCl_3$–aqueous phase; ⊙–C_6H_6 – aqueous phase; 2) – □ – $CHCl_3$ – aqueous phase; △– C_6H_6 –aqueous phase).

The acid dissociation constant of selenoyl-2-acetone determined at an ionic strength of 0.1, and the value obtained, do not contradict conclusions which can be drawn from a comparison of the dissociation constants of analogs of acetylacetone. The dissociation constant of benzoylacetone has been determined polarographically previously by Tachi [12], and also by Eidinoff [13] who measured the pH of partially neutralized solutions of the reagent in aqueous-alcoholic media, containing up 7.4% of ethanol. The value obtained by Tachi ($K_{dissoc.}$ = 3.2 × 10^{-7}) would appear to be high; this might be the result of small amounts of impurities in the test solution. The value found by Eidinoff for the dissociation constant ($pK_{dissoc.}$ = 8.697 ± 0.005) is fairly close to the value we obtained. Some of the deviation in the results may be caused by differences in the conditions used for determining the characteristics studied (different ionic strength of the solution, the presence of an appreciable amount of alcohol, etc.). The value which we found for the dissociation constant of benzoylacetone, namely, $pK_{dissoc.}$ = = 8.96 ± 0.09 does not disagree with the values obtained for the same characteristic for acetylacetone ($pK_{dissoc.}$ = 8.82 [14], $pK_{dissoc.}$ = 8.93 [13] et al), which is an analog of benzoylacetone. The similarity in the structure of selenoyl-2-acetone and acetylacetone explains the comparatively insignificant difference in their dissociation constants. The constancy of the values for the distribution constant of selenoyl-2-acetone and benzoylacetone over a fairly wide concentration range of the reagents in the organic solvent, for the various systems, testifies to the absence of association of reagent molecules in both the aqueous and the organic phases (Fig. 5). Determination of the stability constants, and the distribution constants of the complex compounds of selenoyl-2-acetone and benzoylacetone with various metal ions will assist in assessing the values of these compounds as analytical reagents.

SUMMARY

1. The absorption spectra of aqueous solutions of selenoyl-2-acetone and benzoylacetone at various hydrogen ion concentrations have been studied.

2. The dissociation constants of the reagents indicated have been determined for an ionic strength of the solution of 0.1; $pK_{dissoc.}$ = 8.55 ± 0.08 (selenoyl-2-acetone) and $pK_{dissoc.}$ = 8.96 ± 0.09 (benzoylacetone).

3. The distribution constants of these reagents have been determined in various systems (25 ± 0.1°; $\mu = 0.1$).

a) Selenoyl-2-acetone	$\log K_{distrib.} = 2.922 \pm 0.006$	($CHCl_3 - H_2O$ — phase).
	$\log K_{distrib.} = 3.004 \pm 0.010$	($C_6H_6 - H_2O$ — phase).
b) Benzoylacetone	$\log K_{distrib.} = 3.439 \pm 0.009$	($CHCl_3 - H_2O$ — phase).
	$\log K_{distrib.} = 3.145 \pm 0.010$	($C_6H_6 - H_2O$ — phase).

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THE USE OF A ROTATING PLATINUM MICRO-DISC ELECTRODE IN POLAROGRAPHIC ANALYSIS

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In recent years, in addition to further developments in the theory and practice of polarography with dropping electrodes, there has been a significant increase in the attention displayed by research workers to solid electrodes. Platinum wire electrodes — stationary and rotating — have found the widest application.

The stationary electrode possesses a number of disadvantages which depress its practical value, and limits its applicability. Accordingly, preference is given in analytical practice to the rotating electrode.

The choice of the shape of the electrode, including the wire electrode itself, has not hitherto been given a theoretical foundation. The wire electrode which was first suggested by Kolthoff as long ago as 1941 [1] has been adopted by many research workers, either with or without technical modifications, and has arbitrarily justified itself for solving a number of analytical or electrochemical problems. On the other hand, Levich [2] has given a general quantitative theory of the disc electrode. In the presence of an indifferent electrolyte, the diffusion current which is determined by the reduction of an uncharged particle or ion, is expressed by the equation:

$$i_d = 0{,}62\, n\, FD^{2/3}\omega^{1/2}\nu^{-1/6} cS, \qquad (1)$$

where n is the number of electrons participating in the reaction; F is the Faraday number; D is the diffusion coefficient in cm^2/second; ω is the angular rate of rotation equal to $2\pi m$, where m is the number of rotations of the electrode per second; ν is the kinematic viscosity of the liquid in cm^2/second; c is the concentration of the ions being reduced in moles/ml; and S is the area of the electrode surface in cm^2.

The Levich equation has been checked for the relation between the limiting current and the rotational rate of the electrode by Siver and Kabanov for laminar conditions [3], and by Bagotskaya for turbulent conditions [4]. The authors got good agreement between theory and practice. Siver and Kabanov [5], taking oxygen and hydrogen, found a similar agreement for the relation between the diffusion current and the diffusion coefficient. Hogge and Kraichman [6], and Fedorova and Vidovich [7] confirmed the theory taking the cathodic reduction of iodine as an example. These facts make the disc electrode very attractive for use in analytical practice, and challenges the critical observations of Heyrovskii [8] apropos the use of solid electrodes.

Possible reasons which hinder the practical adoption of the disc electrode, in our opinion, are the complexity of the construction proposed for this electrode, and its relatively large size. Consequent upon this is the rather large size of the apparatus, and the large volume of solution to be polarographed, which, naturally complicates operation. Were the disc electrode given a more practically convenient form, then it could successfully replace the traditional wire electrode, over which it would have undisputed advantages. We have described a disc electrode with such desirable features [9].

The subject of the present article is the study of the characteristics of the micro-disc electrode, and clarification of the possibility of using it for polarographic analysis.

In the work described here, a visual polarograph, and mirror galvanometers type M-21 and GZS with a constant of about 10^{-9} amp./mm were used. In order to avoid working with large amounts of mercury, glycerol or water was introduced into the rotating part of the setup described previously [10] to act as a seal;

contact was established by means of a copper brush (Fig. 1).

Before use, the micro-disc electrode ($S = 0.78\ mm^2$) was polished with emery cloth and cleaned with damp filter paper; it was then washed with water; before introducing the electrode into the solution of ions to be reduced, it was subjected to cathodic polarization for 3-4 minutes in a cell containing 0.1 N hydrochloric or sulfuric acid, at the hydrogen discharge potential (for complete purification of the electrode surface from surface oxides, the presence of which, as pointed out by a number of authors [11-13], complicates the electrochemical process and leads to poorly defined polarographic waves). The anode was a platinum plate with a surface area S of 400 mm^2.

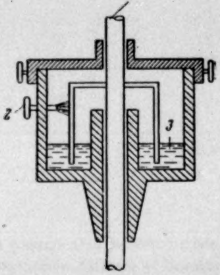

Fig. 1. Seal with rotating electrode, 1) rotating axis; 2) brush contact; 3) glycerol.

Clearly defined, and satisfactorily reproducible waves were obtained for oxygen, hydrogen ions, $[AuCl_4]^-$ and $[PtCl_6]^{2-}$ on the platinum micro-disc electrode (Fig. 2). The wave shown in Fig. 2 were obtained after the tenth cycle without purifying the electrode surface. In this case the maximum deviation from the mean value for the series of determinations did not exceed 3%. In order to get clearly defined and reproducible waves it is essential to center the electrode accurately; it was found necessary that the position of the electrode with respect to its axis did not change from test to test, a condition which it was not difficult to observe.

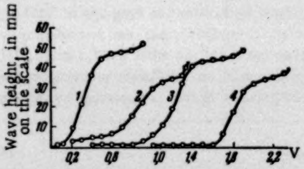

Fig. 2. Waves obtained on a micro-disc electrode. 1) $[AuCl_4]^-$, gold concentration $C_{Au} = 0.775$ mg/25 ml, 1 mm on the scale = 0.09 μa, 800 revolutions/minute; 2) $[PtCl_6]^{2-}$ $C_{Pt} = 2.8$ mg/25 ml, 1 mm scale = 0.36 μa, 800 revolutions/minute; 3) O_2 (saturated solution) 1 mm on the scale = 0.24 μA, 400 revolutions/minute; 4) $[H_3O]^+$ $C_H = 4 \times 10^{-3}$ NH_4Cl, 1 mm on the scale = 2.20 μA, 335 revolutions/minute, supporting electrolyte 0.1 N $NaNO_3$.

In order to verify Levich's equation, the relationship between the diffusion current and the rate of rotation of the electrode was studied. The work was carried out in a supporting electrolyte of 0.1 N $NaNO_3$ at room temperature (20 ± 1°). The following test materials were used: molecular oxygen, hydrogen ions, and $[AuCl_4]^-$. As is evident from Fig. 3, in agreement with theory, the diffusion current is proportional to the square root of the rotational rate of the electrode for all these test materials, including gold, in which case the electrode reactions are accompanied by deposition of metal on the electrode.

A direct proportionality was observed on the micro-disc electrode between the diffusion current and concentration. In Fig. 4 are shown calibration curves we took for hydrogen ions; the calibration curve for gold has been given previously [9].

Using equation (1), values of the diffusion current of hydrogen in a solution of 4×10^{-4} N hydrochloric acid in a supporting electrolyte of 0.1 N $NaNO_3$ were calculated for various rotational speeds of the electrode. The value for the diffusion coefficient of hydrogen ions, taken from the work of Siver and Kabanov [5], was taken as being equal to $7.4 \times 10^{-5}\ cm^2/sec$, while the value assumed for the viscosity was $10^{-2}\ cm^2/sec$. Results of these calculations are given in Table 1.

In evaluating the results obtained it should be borne in mind that the value of the diffusion coefficient which we used holds for several other conditions, and that we did not succeed in achieving strict centering of the electrode. Taking these facts into account, and also the small value of the electrode surface, the agreement obtained between the experimental and theoretical values can be regarded as satisfactory.

On the basis of the experimental results which we obtained for gold, an attempt was made, using equation (1), to calculate the value of the diffusion coefficient for $[AuCl_4]^-$ ions in a supporting electrolyte of

0.1 N $NaNO_3$. Results of these calculations are given in Table 2.

The value which we found for the diffusion coefficient of the $[AuCl_4]^-$ ion (Table 2) is in satisfactory agreement with the value of 1.04×10^{-5} cm^2/sec^{-1}, found by other authors by means of a dropping electrode and using the Il'kovich Equation [15].

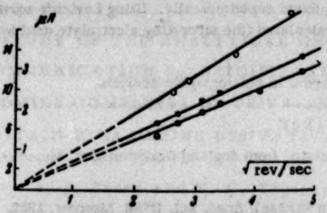

Fig. 3. The relation between the diffusion current and the rotational speed of the micro-disc electrode. O) oxygen, saturated solution, ⊚) hydrogen 4×10^{-4} N HCl; ⊕) gold, 1.6×10^{-4} M, solution of $H[AuCl_4]$ (the values of 1-3 μa relate to gold, supporting electrolyte 0.1 N $NaNO_3$).

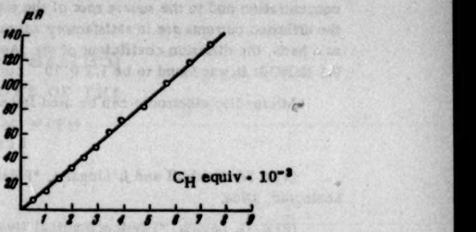

Fig. 4. Relation between diffusion current and hydrogen ion concentration.

As our experiments showed, the micro disc can also be used for polarography in a flow stream. The possibility of carrying out polarographic analysis in a flow has been investigated by Wilson and Smith [14] using a dropping mercury electrode. A solid micro-disc electrode may prove better for this purpose, particularly when it is considered in conjunction with automation of control.

TABLE 1

m = rev per sec	ω = 2πm	$\omega^{\frac{1}{2}}$	i_d, calc., in μA	i_d found exp. in μA	Deviation, in %
5,60	35,2	5,94	8,3	7,4	10,5
7,25	45,5	6,75	9,4	7,7	18,0
9,60	60,3	7,76	10,8	9,1	15,5
11,75	73,8	8,60	12,0	9,85	18,0
22,75	142,0	11,90	16,6	13,9	16,0

The platinum micro-disc electrode has a number of advantages over the wire electrode. The first is simpler to handle. Periodical chemical or mechanical cleaning of the wire electrode (for removal of electrode reaction products from its surface) leads to fairly rapid corrosion of the electrode and to breakage. A micro-disc electrode can be cleaned much more easily, particularly by light polishing on a file or on fine emery paper. This leads to complete renewal of the electrode surface without destroying its completeness, thanks to which its period of service is much longer.

TABLE 2

$\omega^{\frac{1}{2}}$	i_d, in μA	$D[AuCl_4]^-$ in $cm^2/sec \cdot 10^5$
5,94	1,35	1,04
6,75	1,70	1,20
7,76	1,98	1,24
2.60	2,16	1,21
10,10	2,52	1,19
11,90	3,15	1,27
	Mean	1,19

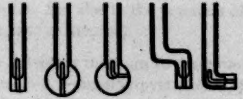

Fig. 5. Forms of the micro-disc electrode.

Moreover, it should be noted that by making the glass sheath of the electrode in various shapes (Fig. 5), it is possible to modify the diffusion conditions and the stirring conditions.

SUMMARY

The possibility of using a rotating micro-disc electrode in polarographic analysis has been investigated. In accordance with Levich's equation, diffusion currents on the micro-disc electrode are proportional to the concentration and to the square root of the rotational speed of the electrode; the values found theoretically for the diffusion currents are in satisfactory agreement with those found experimentally. Using Levich's equation as a basis, the diffusion coefficient of the $[AuCl_4]^-$ ions was calculated (the supporting electrolyte used was 0.1 $NaNO_3$); it was found to be 1.2×10^{-5} cm^2/sec.

Micro-disc electrodes can be used instead of wire electrodes in polarographic analysis.

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A STUDY OF THE ANALYTICAL CHEMISTRY OF THALLIUM COMMUNICATION 2. PRECIPITATION REACTIONS OF THE BROMIDE COMPLEXES OF TRIVALENT THALLIUM WITH CERTAIN PYRAZOLONE DERIVATIVES*

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On the basis of the values for the normal oxidation–reduction potentials $E_{0\,Tl^{3+}/Tl^{+}} = 1.22$ volt and $E_{0\,Br_2/Br^-} = 1.066$ volt [1], it might be assumed that trivalent thallium ions would oxidize bromine ions, even though only partially, to elemental bromine. Nevertheless, even qualitative tests show that in acid solution (2 N H_2SO_4) this reaction does not occur. This fact can be explained on the basis that trivalent thallium ions form stable complex ions with bromine, as a result of which the oxidation potential of the system Tl^{3+}/Tl^{+} drops sharply. Benoit [2] using a potentiometric method found the following pK values: 9.7 for $TlBr^{2+}$, 6.9 for $TlBr_2^{+}$, 4.6 for $TlBr_3$, 2.7 for $TlBr_4^{-}$. Peshanskaya and Vallada-Dubois [3], on the basis of spectrophotometric and potentiometric measurements, have concluded that in solutions containing Tl^{3+} and Br^-, the following complex ions exist: $TlBr^{2+}$ (pK_1 8.9), $TlBr_2^{+}$, (pK_2 7.5), $TlBr_3$ (pK_3 5.7), $TlBr_4^{-}$ (pK_4 4), $TlBr_5^{2-}$ (pK_5 3.1), $TlBr_6^{3-}$ (pK_6 2.4). The values found for pK show that the bromide complexes of thallium are quite stable, the stability decreasing with increasing coordination number.**

It has been established that Tl^{3+} ions, in the presence of Br^- and Cl^- ions, interact with basic dyes to give sparingly soluble compounds. Thus, Feigl and co-workers [5] have shown that the bromide and chloride complexes of thallium form red-violet precipitates with the basic dye rhodamine B; these precipitates can be extracted with organic solvents to give intensely red-colored extracts; the reagent itself is not extracted. A similar color reaction is given in weakly acid solutions by the complex anions $TlCl_4^-$ and $TlBr_4^-$ with methyl-violet [6, 7] and other basic dyes of the diaminotriphenylmethane series [8, 9]. A method has been developed for separating $10^{-6} - 10^{-7}$% Tl based on the coprecipitation of $TlCl_4^-$ with a precipitate formed by p-dimethylaminoazobenzene and sodium p-dimethylaminoazobenzene-p-sulfonate [10]. There are published references [11, 12] to the detection of univalent thallium by means of a very sensitive reaction based on the formation of characteristic crystals by the action of a solution containing sodium iodide and iodine (oxidizing agent) in the presence of concentrated hydrochloric acid and several alkaloids, and also in the presence of certain nitrogen-containing organic bases (quinoline, antipyrine, pyramidone, and urotropine).

Our experiments have shown that, under certain conditions, trivalent thallium in the presence of bromine ions is precipitated by pyrazolone derivatives: antipyrine (1-phenyl-2,3-dimethylpyrazolone), pyramidone (dimethylaminoantipyrine), diantipyrylmethane, and diantipyrylphenylmethane.

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*For Communication 1, see J. Anal. Chem. 13, 180 (1958). Original Russian pagination. See C.B. Translation.

**The bromide complexes of trivalent thallium are stable enough to permit amperometric titration of Tl^{3+} ions with potassium bromide. Songina [4] has carried out such a titration. Nevertheless, on the basis of a comparison of the oxidation–reduction potentials, she erroneously suggested that the reaction: $Tl^{3+} + 2Br^- \rightarrow Tl^{+} + Br_2$ forms the basis of the method she had developed. Experiments show that under the titration conditions used in Songina's method, liberation of elemental bromine is not observed.

The aim of our work was the study of the precipitation reactions of the bromide complexes of thallium with certain pyrazolone derivatives from the point of view of the analytical application of such reactions. Accordingly, we were interested in the properties of the compounds formed, their composition, their suitability for gravimetric purposes, and the possibility of developing methods for the amperometric titration of thallium.

1. Precipitation of Trivalent Thallium in the Presence of Bromide Ions with Pyramidone

On addition of an aqueous solution of pyramidone to an acid solution containing Tl^{3+} ions and an excess of bromide ions, there is formed a white, clotted precipitate with a yellow tinge. In order to study the properties and composition of the precipitate the latter was isolated and analyzed.

For preparation of the bromide complex of thallium with pyramidone, about 0.5 g of $TlNO_3$ dissolved in 1 N H_2SO_4 was oxidized with $(NH_4)_2S_2O_8$; to the solution thus obtained was added 5 ml of a 40% solution of HBr, and 0.5 g of pyramidone dissolved in dilute H_2SO_4. The yellowish-white material which was formed was filtered off, and then washed 2-3 times with water. On crystallizing from acetone, large crystals with a bright-yellow color and in the form of right hexahedrons, were obtained. The crystals melted at 185° with decomposition.

In weakly acid solution, trivalent thallium oxidizes pyramidone to form an intensely blue-violet colored solution; the color is not stable, but the color effect produced can serve for the qualitative detection of Tl^{3+} in the absence of an oxidizing agent. Tl^{3+} can be detected as follows: to 2-5 ml of a weakly acid solution (pH 3-4, in the absence of Cl^- and Br^- ions) is added 1 ml of a saturated solution of pyramidone. Immediately, or almost immediately, there appears a blue-violet color which disappears on standing. Limit of identification 4 γ/ml.

Independently from us, the oxidation of pyramidone by trivalent thallium was used by Kamemoto [13] for the photometric determination of 1-5 mg of Tl in 50 ml of solution at 510 mμ. He showed that at pH 4.0, the color gradually changes from violet to red, and after 60 minutes becomes almost constant. At considerably lower Tl concentrations we did not observe this change of color to red, since it is several times less intense than the colors observed by Kamemoto. In the presence of large amounts of Cl^- and Br^-, at pH 4-5, the color is accompanied by the formation of a precipitate, nevertheless, its intensity is less than in the case where Cl^- and Br^- are absent. The pH value at which the color appears in the presence of Cl^- and Br^- is somewhat higher than in their absence.

The compound formed between thallium and pyramidone was analyzed for its Br and Tl contents. Bromine was determined, after dissolving an exact aliquot of the material in acetone, by precipitation with $AgNO_3$ and weighing the AgBr formed. Thallium was determined gravimetrically as TlI; an aliquot of the test material was dissolved in a small amount of acetone, about 0.1 g of KI was added and a few ml of 5% $Na_2S_2O_3$ then added until the yellow color of the solution disappeared; the solution plus precipitate was then allowed to stand overnight; the precipitate was filtered through a No. 3 glass crucible, washed with 80% acetone, and finally dried at 120-130° and weighed.

Found: Br 41.88; 42.45; 42.10%; Tl — 27.17; 26.90; 26.72%. Calculated for $C_{13}H_{17}ON_3 \cdot HTlBr_4$: Br — 42.26%; Tl — 27.02%.

On the basis of the results obtained it can be postulated that the reaction proceeds according to the following equation:

$$C_{13}H_{17}ON_3 + Tl^{3+} + 4Br^- + H^+ \rightarrow C_{13}H_{17}ON_3 \cdot HTlBr_4.$$

Despite the relatively high molecular weight of tetrabromothalliumpyramidone (756.4) and the favorable conversion factor to Tl (F = 0.2702), this compound is not suitable for the quantitative determination of thallium because of its appreciable solubility in water. Thallium is not quantitatively precipitated at very high concentrations of bromide and pyramidone. The thallium compound is soluble in many organic solvents: acetone, ethanol, chloroform, carbon tetrachloride, etc.

2. Precipitation of Trivalent Thallium in the Presence of Bromide Ions with Antipyrine

Thallium is precipitated by antipyrine from an acid solution, at sufficiently high bromide concentrations, in the form of a finely dispersed turbidity; crystals appear on agitation. The crystals, which are almost colorless when they are formed, become greenish-yellow after filtration and drying. The material is appreciably soluble in water, alcohol, and ether; it is readily soluble in acetone and chloroform, and insoluble in excess precipitant. On recrystallizing from acetone, yellowish needles which melt at 129-130° are formed.

The compound was synthesized by the same method as that described in the previous case. In addition to determining Br and Tl, the molar ratio of Tl^{III}: antipyrine was established by determining the excess antipyrine in solution after precipitation of an exactly known amount of Tl by a known amount of antipyrine. This was done as follows: to a solution of 17.90 mg of Tl^+ contained in a 50 ml standard flask was added 2 ml of 2 M KBr, 2 ml of HNO_3 (1 : 1), and 3 ml of 0.1 N $KBrO_3$; excess bromine was removed by addition of 1-2 drops of a 10% solution of sulfosalicylic acid; 10 ml of 0.1044 M antipyrine solution containing 1 mole/liter of KBr was then added and the solution made up to the mark. The following day the precipitate was filtered off through a dry filter into a dry beaker. Antipyrine was determined in the filtrate by a somewhat modified Gusev method [14], an aliquot (10 ml) of the solution was transferred to a dry beaker, and 10 ml of 0.02357 M $K_4Fe(CN)_6$ and 10 ml of 1 N H_2SO_4 added. After mixing the whole thoroughly, it was allowed to stand for 10-15 minutes and the solution then filtered through a dry filter into a dry beaker. 15 ml of this filtrate was taken for titration, this volume was diluted with water to 50-75 ml and then 1-2 ml of 1% $K_3Fe(CN)_6$ added and the solution titrated potentiometrically with a standard $ZnCl_2$ solution. In this way excess ferrocyanide was determined, and from this the amount of antipyrine in the solution above the precipitate of the bromide complex of thallium with antipyrine. The antipyrine solution was also standarized by the ferrocyanide method. In two such experiments 0.1965 g of antipyrine and 0.0179 of Tl were taken in each case. The excess antipyrine found was 0.1646 and 0.1609 g. These values correspond to molar ratios of Tl : $C_{11}H_{12}ON_2$ of 1 : 1.94 and 1 : 2.16. It can be assumed therefore that 1 mole of Tl is associated in the complex with 2 moles of antipyrine.

The bromine content of the compound obtained was determined by weighing the bromine as AgBr, and also by potentiometric titration of the solution obtained by dissolving the material in a 1 : 1 mixture of water and acetone, using silver nitrate as the titrant and using a silver electrode.

Found: Br 35.89 (potentiometrically) 35.49; 35.62 (gravimetrically) Tl 22.60; 22.14% (gravimetrically)
Calculated: for $(C_{11}H_{12}ON_2)_2HTlBr_4$: Br — 35.46%; Tl — 22.68%.

Thus, the reaction proceeds according to the equation:

$$2C_{11}H_{12}ON_2 + H^+ + 4Br^- + \rightarrow (C_{11}H_{12}ON_2)_2 \cdot HTlBr_4.$$

Gravimetric determination of Tl by precipitation and weighing as $(C_{11}H_{12}ON_2)_2 \cdot HTlBr_4$ was carried out as follows: to the solution containing Tl^+ was added 5 ml of HNO_3 (1 : 1), a few ml of 0.01 N $KBrO_3$ (1 ml per 10 mg Tl), and 10 ml of 2 M KBr; excess bromine was removed by addition of a 10% solution of sulfosalicylic acid; 10-15 ml of 0.1 M antipyrine was then added slowly with sitrring. The total volume amounted to 40-50 ml. After standing for a short time the precipitate was filtered through a No. 3 glass filter, and washed 2-3 times, first with a solution of precipitant, and then with a saturated solution of the compound formed; the precipitate was finally dried at 105-110°. The precipitate was not hygroscopic and reached constant weight after 1 hour.

The method gives results which are systematically 2-3% low (Table 1), probably because of the appreciable solubility of the precipitate under the experimental conditions used. In the absence of excess precipitant the precipitate is appreciably soluble; accordingly, amperometric titration of the bromide complex of thallium with a solution of antipyrine is not possible.

3. Precipitation of Trivalent Thallium in the Presence of Bromide By Means of Diantipyrylmethane

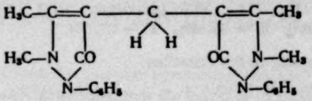
On the assumption that the solubility of a compound decreases with increasing molecular weight, we hoped that we would get more satisfactory results by using diantipyrylmethane, which has a higher molecular weight, for precipitating the bromide complex of thallium.

The reagent was synthesized by Zhivopistsev's method [15]. It was purified as follows: about 2 g of material was dissolved in 200 ml water on addition of 3-4 ml of concentrated HCl, and the solution obtained was neutralized with NH_4OH (1 : 1) while stirring. The precipitated base was filtered, and then washed until it gave a negative test for chloride ions. The purified crystallohydrate had a melting point of 143°. A 1% solution of the reagent in 0.5 N H_2SO_4 containing 1% of HBr (by weight) was used for gravimetric determinations: 1 ml of this solution precipitates about 5 mg of Tl. A 0.1% solution of diantipyrylmethane, prepared by dissolving an exactly weighed aliquot of the reagent dried to constant weight at 105-110°, was used for amperometric titration. The solution was standardized by means of an iodometric method similar to that used by Kumov [16] for determination of antipyrine, since the molecule of diantipyrylmethane contains two atoms of hydrogen which can be replaced by iodine. For this purpose, 10 ml of 0.005 N I_2 and 0.1 g of CH_3COONa were added to 5 ml of the diantipyrylmethane solution; after 3-5 minutes excess iodine was titrated amperometrically at 0 volt with 0.005 N $Na_2S_2O_3$ until the iodine current disappeared. It was found that 1 ml of this solution contained 0.7997 mg of antipyrylmethane, or based on the aliquot taken, 1 ml of this solution contained 0.8010 mg.

TABLE 1

Gravimetric Determination of Thallium as $(C_{11}H_{12}ON_2)_2 \cdot HTlBr_4$

Weight of precipitate of $(C_{11}H_{12}ON_2)_2 \cdot HTlBr_4$	Tl taken, in mg	Tl found, in mg	Error	
			in mg	in %
119,7	26,8	27,2	+0,4	+1,5
119,0	26,8	27,0	+0,2	+0,7
152,1	35,8	34,5	+1,3	—3,6
153,6	35,8	34,8	—1,0	—3,0
191,8	44,7	43,5	—1,2	—2,7
197,3	44,7	44,8	+0,1	+0,2
77,5	17,7	17,6	—0,1	—0,6
76,8	17,7	17,4	—0,3	—1,8
57,3	13,3	13,0	—0,3	—2,3
37,5	8,84	8,50	—0,34	—3,8
39,3	8,84	8,93	+0,09	+0,1



We established that diantipyrylmethane quantitatively precipitates thallium from solutions containing bromide ions. The clotted precipitate formed externally resembles silver bromide; on agitation it rapidly coagulates.

In order to determine the composition of the bromide complex of thallium with diantipyrylmethane, a solution containing a known amount of Tl^{3+} was titrated amperometrically at a sufficient concentration of bromide ions (1 mole/liter KBr) with an accurately prepared solution of diantipyrylmethane. The equivalence point was established by the disappearance of the reduction current of thallium on a rotating platinum microelectrode at a potential of 0.0 v with respect to the saturated calomel electrode (Fig. 1, a,b). Titration results (Table 2) showed that diantipyrylmethane and thallium —as its bromide complex—react in a molar ratio approximating to unity.

The bromine content of the synthesized compound was determined by potentiometric titration of an aliquot of the compound, dissolved in 9 : 1 mixture of acetone and water, with silver nitrate. Thallium was determined by complexometric titration, after decomposition of an aliquot of the compound with concentrated H_2SO_4 in the presence of H_2O_2, using 1-(2-pyrydylazo)-2-naphthol as indicator [17].

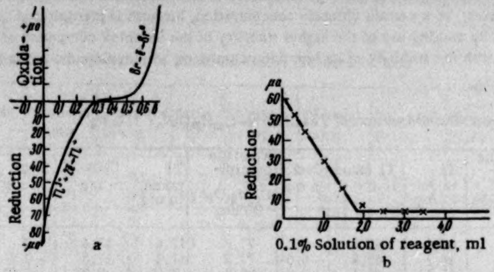


Fig. 1. a) Current-voltage curve for 1.25×10^{-3} N $Tl_2(SO_4)_3$ in a supporting electrolyte of 1 M KBr; b) Amperometric titration curve for the bromide complex of trivalent thallium with a solution of diantipyrylmethane.

Found: Br 34.57; 34.81%; Tl 22.36; 22.43%. Calculated for $C_{23}H_{24}O_2N_4 \cdot HTlBr_4$: Br 34, 98%, Tl 22.38%.

Accordingly, the composition of the bromide complex with diantipyrylmethane corresponds to the formula:

$$C_{23}H_{24}O_2N_2 \cdot HTlBr_4.$$

Gravimetric determination of thallium by precipitation and weighing as $C_{23}H_{24}O_2N_2 \cdot HTlBr_4$ was carried out as follows: to an acid solution of Tl^{3+} sulfate or nitrate was added a 1% solution of the reagent and some HBr (1-2 ml for each 5 mg of Tl); the precipitate was filtered through a No. 3 glass filter and washed with HBr solution (1 : 100); it was then dried at 100-120° to constant weight. The results are given in Table 3. The conversion factor to thallium is 0.2238.

TABLE 2

Molar Ratios of Diantipyrylmethane and Thallium

Thallium taken			Diantipyrylmethane used			Molar ratio Tl^{III} $C_{23}H_{24}O_2N_2$
ml (0.262 mg/ml)	in mg	mmoles (× 10^{-3})	ml (0.01 mg/ml)	in mg	mmoles (× 10^{-3})	
2,00	0,524	2,56	1,15	0,921	2,37	1 : 0,9
3,00	0,786	3,85	1,90	0,522	3,83	1 : 1,0
3,00	0,786	3,85	1,90	1,522	3,83	1 : 1,0
5,00	1,310	6,42	3,10	2,483	6,40	1 : 1,0
5,00	1,310	6,42	3,15	2,528	6,52	1 : 1,0
5,00	1,310	6,42	3,12	2,500	6,44	1 : 1,0

Elements such as zinc and copper, which do not form stable bromide complexes, do not cause any difficulty during the determination of thallium, since they are not precipitated by diantipyrylmethane. It is known, however, [17] that at relatively high bromide concentrations cadmium reacts with the reagent. Nevertheless, in the absence of excess bromide ions, this metal is found in the form of the bromide complexes $CdBr^+$ and $CdBr_2$ which are not precipitated by diantipyrylmethane. Experiments showed that thallium can be determined in the presence of fairly large amounts of cadmium (Table 4), as long as precipitation is carried out from solutions free from bromide ions, by adding the reagent and HBr in amounts which are twice the theoretical amounts necessary for forming $TlBr_4^-$ ions. Bismuth, even under these conditions, is coprecipitated with thallium to a considerable extent as a consequence of the higher stability of its bromide complexes as compared with those of the cadmium complexes; at a certain chloride concentration, bismuth is precipitated quantitatively by diantipyrylmethane [18]. By making use of the higher stability of the complex compound of bismuth with Complexon III as compared with the stability of its bromide complexes, we developed a technique for the determination of Tl^{3+} in the presence of bismuth, in which the bromide complex of thallium was precipitated with diantipyrylmethane in the presence of Complexon III in a weakly acid medium (pH about 2). To the solution containing Tl^{3+} and Br^{3+} was added a few ml of a 5% Complexon III solution (1 ml per 20 mg), this was followed by addition of ammonia until the solution had a weak odor of the latter (if, at this stage, a turbidity should appear, some more Complexon III should be added), the necessary amount of reagent was then added and the solution carefully acidified with 2 N H_2SO_4 until the color of tropeoline 00 changed from yellow to orange red; the precipitate formed was washed twice with 0.5% Complexon III solution and then 2-3 times with HBr (1 ; 100) solution. The method gave satisfactory results (Table 4). In order to prevent interference from Sb^V which forms stable bromide complexes which are precipitated by diantipyrylmethane, the antimony was complexed with tartaric acid; this complex is stable during subsequent acidification. This technique permits determination of thallium in the presence of antimony (Table 4).

TABLE 3

Gravimetric Determination of Thallium as $C_{23}H_{24}O_2N_4 \cdot HTlBr_4$

Wt. of the precipitate $C_{23}H_{24}O_2N_2 \cdot HTlBr_4$	Tl taken, in mg	Tl found, in mg	Error, in mg	Wt. of the precipitate $C_{23}H_{24}O_2N_2 \cdot HTlBr_4$	Tl taken, in mg	Tl found, in mg	Error, in mg
203,7	45,7	45,6	—0,1	77,6	17,4	17,4	0
201,5	45,7	45,1	—0,6	77,3	17,4	17,3	—0,1
206,0	45,7	46,1	+0,4	38,8	8,70	8,69	—0,01
116,3	26,0	26,0	0	38,3	8,70	8,57	—0,13
115,9	26,0	25,9	—0,1	39,3	8,70	8,80	+0,10
117,4	26,0	26,3	+0,3	35,1	7,84	7,86	+0,02
				35,0	7,84	7,84	0

TABLE 4

Gravimetric Determination of Thallium in the Presence of Zinc, Copper, Cadmium, Bismuth, and Antimony

Tl taken, in mg	Added, in mg	Tl found, in mg	Ratio Tl : Me	Tl taken, in mg	Added, in mg	Tl found, in mg	Ratio Tl : Me
9.15	575 Zn	9,11	1 : 60	9,15	3067 Cd	9,11	1 : 343
7,32	1977 Zn	7,50	1 : 200	7,32	80 Bi	7,25	1 : 10
9.15	1786 Cu	9,25	1 : 195	7,32	230 Bi	7,19	1 : 100
7,32	1786 Cu	7,38	1 : 244	7,32	100 Sb	7,43	1 : 14
9,15	86 Cd	9,02	1 : 10	6,40	100 Sb	6,49	1 : 15
9,15	1276 Cd	9,20	1 : 139	9,15	200 Sb	9,16	1 : 22
7,32	3067 Cd	7,36	1 : 419				

Among those elements which interfere is Fe^{III} which forms an intensely red colored solution with the reagent; the thallium precipitate is accordingly heavily contaminated with iron. Interference from iron can be avoided by precipitating thallium from a weakly acid solution containing the necessary amount of Complexon III for complexing the iron.

Determination of thallium in the presence of iron was carried out as follows: to the solution containing Tl^{III} and Fe^{III} was added a 5% solution of Complexon III (5 ml per 30 mg Fe), this was followed by addition of NH_4OH until the appearance of a dark-red color, this is a sign of the complete complexing of iron by Complexon III; a few drops of 1 N H_2SO_4 was then added until the red color of the liquid changed to orange, about 5 ml of reagent solution was next added with stirring, finally, 10 N H_2SO_4 was added dropwise until precipitate had ceased to separate out (it cannot be assumed that the appearance of a red color testifies to the decomposition of iron complexonate). For ratios of Tl : Fe > 1 : 10, precipitation must be repeated. For this purpose the precipitate was washed with dilute HBr (1 : 100), containing 0.5% Complexon III, the precipitate was then washed off the filter with 50-75 ml of an ammoniacal solution of Complexon III having a pH of 8-9, 5 ml of reagent was added and the solution acidified with 10 N H_2SO_4; under these conditions an absolutely white flocculent precipitate was obtained, this was filtered off, washed, dried, and weighed (Table 5).

TABLE 5

Gravimetric Determination of Thallium in the Presence of Iron

Tl taken, in mg	Tl found, in mg	Fe added, in mg	Ratio Tl:Fe	Tl taken, in mg	Tl found, in mg	Fe added, in mg	Ratio Tl:Fe
7,42	7,48	20	1 : 3	7,32*	7,40	200	1 : 28
8,24	8,39	40	1 : 5	6,40*	6,31	200	1 : 30
8,24	8,30	40	1 : 5	6,40*	6,34	320	1 : 50
7,32	7,23	75	1 : 10	6,40*	6,18	400	1 : 62
7,32	7,49	100	1 ; 14				

*The thallium was reprecipitated.

TABLE 6

Amperometric Determination of Thallium (volume of solution 15 ml)

Tl taken, in mg	Tl found, in mg	Error		KBr concentration, in mole/liter
		mg	%	
1,05	1,05	0	0	1,0
1,05	1,05	0	0	0,002
1,31	1,31	0	0	1,3
1,31	1,29	−0,02	−1,5	1,3
0,66	0,68	+0,02	+3,0	Saturated solution
0,66	0,65	−0,01	−1,5	1.7
0,52	0,50	−0,02	−4,0	1,6
0,92	0,89	−0,03	−3,3	1,5
0,92	0,92	0	0	0,1
0,92	0,90	−0,02	−2,2	Saturated solution
1,31	1,32	+0,01	+0,8	
1,31	1,30	−0,01	−0,8	0,002

In addition to determining thallium gravimetrically by means of this reagent, it is also possible to determine it amperometrically under the conditions described above. Changes in potassium bromide over a wide range have no effect on the titration results, titration can be carried out both in a saturated solution of KBr, and in a solution containing KBr in an amount of only 30-50% greater than that theoretically necessary for formation of $TlBr_4^-$ ions (Table 6).

Thallobromic acid is obviously a strong acid, since the solubility of its salts with diantipyrylmethane does not change appreciably with increasing H_2SO_4 concentration, and titration can accordingly be carried out in strongly acid solutions (Table 7). Cadmium present to the extent of ten times that of thallium does not interfere with determination of the latter, as long as the bromide ion concentration is not greater than 0.1 M; similarly, no interference is shown by copper, zinc, bismuth, and iron, when the latter is complexed by means of Complexon III (or, not quite so well, with fluoride ions) so as to eliminate interference from the cathodic current of the Fe^{III} ion at 0 volt. Some results for amperometric titration are given in Table 8.

TABLE 7

Amperometric Determination of Thallium at Various H_2SO_4 Concentrations of the Solution

Tl taken, in mg	Tl found, in mg	Error		H_2SO_4 concentration, in mole/liter
		in mg	in %	
0.66	0.67	+0.01	+1.5	0.5
0.66	0.65	−0.01	−1.5	0.5
0.66	0.66	0	0	1.0
1.31	1.31	0	0	1.0
0.66	0.67	+0.01	+1.5	3.0
0.92	0.91	−0.01	−1.1	3.0
0.79	0.79	0	0	5.0
0.79	0.80	+0.01	+1.2	10.0

An increase in KBr concentration to a level higher than that indicated in Table 8 leads to appreciable coprecipitation of bismuth, and the results for thallium are much too high.

4. Precipitation of Trivalent Thallium in the Presence of Bromide Ions with Diantipyrylphenylmethane

The reagent was synthesized by Gusev's method [19]. The bromide complex of thallium with diantipyrylphenylmethane was synthesized as follows: an aliquot of $TlNO_3$ (0.5328 g) was dissolved in 50-100 ml of 1 N H_2SO_4, and the thallium oxidized with $(NH_4)_2S_2O_8$ (Excess of the oxidizing agent was removed by boiling); 5 ml of 40% HBr was then added, followed by 0.87 g of diantipyrylphenylmethane dissolved in 25 ml of glacial acetic acid. The bright-yellow precipitate which separated out was filtered off and washed with water. The precipitate was purified by recrystallization from a mixture of methanol and acetone. The recrystallized material was in the form of lemon-yellow needles. At temperatures greater than 220° the material darkened in color, but did not melt (pressumably decomposition occurred). The properties of the compound obtained were similar to those of the three compounds described above: $C_{13}H_{17}ON_3 \cdot HTlBr_4$, $(C_{11}H_{12}ON_2)_2 \cdot$ $\cdot HTlBr_4$, $C_{23}H_{24}O_2N_4 \cdot HTlBr_4$.

TABLE 8

Amperometric Determination of Thallium in the Presence of Other Metals (in a supporting electrolyte of 2 N H_2SO_4)

Tl taken, in mg	Me added, in mg		Tl found, in mg	Error, in mg	KBr concentration, in mole/liter
0,79	100	Zn	0,80	+0,01	0,002
1,31	50	Zn	1,31	0	0,002
0,66	200	Zn	0,66	0	0,002
0,79	70	Bi	0,78	−0,01	0,002
0,79	100	Bi	0,80	+0,00	0,002
1,31	10	Cd	1,29	−0,02	0,002
0,79	50	Cd	0,79	0	0,002
0,79	10	Cd	0,80	+0,01	0,1
0,79	10	Cd	0,79	0	0,1
0,79	10	Cd	0,84	+0,05	0,2
0,79	10	Cd	0,86	+0,07	0,2
0,79	20	Cd	0,91	+0,12	0,5

During an analysis of the recrystallized material it was found gravimetrically that its bromine content was 32.56 and 32.84%, while the thallium content was found to be 20.84 and 20.62% by a complexometric method. The theoretical bromine and thallium contents for $(C_{11}H_{11}ON_2)_2\ CHC_6H_5 \cdot HTlBr_4$ were 32.29% Br, and 20.65% Tl.

An attempt was made to use this reagent for the gravimetric determination of thallium in which a 1% solution of diantipyrylphenylmethane in glacial acetic acid containing 1% HBr was used for precipitation. Satisfactory results were not obtained, however, because of the slight solubility of the reagent in water, and also because of the low solubility of the bromide of diantipyrylphenylmethane, as a result of which the latter is strongly coprecipitated with the precipitate of $(C_{11}H_{11}ON_2)_2CHC_6H_5 \cdot HTlBr_4$.

SUMMARY

1. Trivalent thallium ions can be precipitated in the presence of bromide ions by pyramidone, antipyrine, diantipyrylmethane, and diantipyrylphenylmethaneto form compounds whose composition corresponds to the following formulas: $C_{13}H_{17}ON_3 \cdot HTlBr_4$, $(C_{11}H_{12}ON_2)_2 \cdot HTlBr_4$, $C_{23}H_{24}O_2N_4 \cdot HTlBr_4$, $(C_{11}H_{11}ON_2)_2CHC_6H_5 \cdot HTlBr_4$.

2. Some of the properties of the compounds listed above have been studied.

It has been shown that $C_{13}H_{17}ON_3 \cdot HTlBr_4$, $(C_{11}H_{12}ON_2)_2 \cdot HTlBr_4$, $C_{23}H_{24}O_2N_4 \cdot HTlBr_4$ are not suitable for the determination of thallium; using $C_{23}H_{24}O_2N_4 \cdot HTlBr_4$, however, it is possible to develop gravimetric and amperometric methods for determining thallium in the presence of other elements (Cu, Zn, Cd, Bi, Fe, and Sb).

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THE POLAROGRAPHIC DETERMINATION OF INDIUM

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Despite the fact that many methods have already been suggested for the quantitative determination of indium (spectrographic [1-3], titrimetric [4], colorimetric [5], polarographic [6], etc.), there is at the moment, no rapid and reliable method for the determination of this element; such a method is of particular importance for the technical production of indium, and for its determination in materials during the search for indium raw materials.*

The most widely used method is the polarographic method suggested by Aref'eva [7]; however, the chemical preparation of the solutions to be polarographed is very long, difficult, and incomplete.

In particular, according to Gurin's results [8], in order to achieve complete separation of cadmium from indium by means of ammonia, at least a threefold reprecipitation is necessary for ordinary industrial materials. At the same time it is essential to completely remove copper, and particularly cadmium, from the indium solution because of the nearness of their half-wave potential.

Various other methods have been suggested for preparing the solutions for polarographic determination of indium [9-11].

We should like to suggest an amalgam method for preparing the solutions for polarographing, for the determination of indium in production materials and wastes containing hundredth parts of a percent, and more, of indium. A characteristic feature of this technique is that during treatment of the original sulfuric acid solution of indium (at ordinary temperatures) with the zinc amalgam, all those elements which interfere with the polarographic determination of indium are removed, while the indium remains in solution. To the solution purified in this way is added 10% of its weight of sodium chloride and the indium then determined polarographically. Removal of indium from a number of elements, including tin and cadmium, in sulfuric acid solutions on a zinc amalgam, is based on the specific behavior of indium towards the sulfate ion.

In 1947, a study was made of the effect of chlorides on the value of the diffusion current for indium in sulfuric acid solutions [13]. It was established that addition of chloride ions until their concentration is 10% of the sulfuric acid solution, in which the polarographic wave for indium cannot be detected, ensures the normal reduction of indium ions and the appearance of its wave. Other research workers have observed the same phenomenon at various times: Kolthoff and Lingane [14], Babko, Polishchuk, and Volkova [15], Bukhman [16]. Seward [17] and Ensslin [18], in the system indium sulfate—sulfuric acid established that an acid sulfate of indium with the composition $In_2(SO_4)_3 \cdot H_2SO_4 \cdot 7H_2O$ is formed. Muzyka [19] while studying the same system by electroconductivity, cryoscopic, and transport-number methods established the existence of the anion $[In(SO_4)_2]^-$ in solution. Aksel'rud [20] using a polarographic method, confirmed the existence of the indium anion $[In(SO_4)_2]^-$ in acid solutions. Thus, the reason for the slow reduction of indium ions from sulfuric acid solutions is the formation of complex indium anions, and the changes in the value of the reduction potential of the latter arising from this. Under such conditions, as we have established, this process is essentially independent of the nature of the cation (hydrogen or metal) in the sulfates taken (Table 1).

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*For a review of methods of determining indium, see [6a].

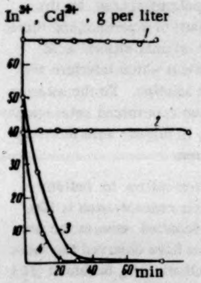
The half-wave potential of indium in a hydrochloric acid solution is equal to −0.597 volt (with respect to the saturated calomel electrode), while in sulfuric acid it is −1.06 volt; the half-wave potential of cadmium in sulfuric acid is equal to −0.642 volt. The large difference between the values of the potentials makes it comparatively simple to separate indium and cadmium completely in sulfuric acid solution by means of a zinc amalgam. The results obtained are shown in the diagram.

TABLE 1

Effect of the Concentration of SO_4^{2-} Ions on the Extent of Reduction of Indium on a Zinc Amalgam

In H_2SO_4 solutions		In solutions of sulfates*		
H_2SO_4 concentration, in %	Extent of the reduction of indium, in %	Sulfate taken	Concentration of SO_4^{2-} ions, in %	Extent of the reduction of indium, in %
3	12.1	$(NH_4)_2SO_4$	20.0	Not reduced
6	9.5	$MgSO_4$	19.9	*
10	5.8	$MnSO_4$	20.2	*
15	2.4	$ZnSO_4 \cdot 7H_2O$	21.0	*
20	Not reduced	—	—	*

*In order to avoid hydrolysis, about 1.5% of free sulfuric acid was added to the solution.



Separation of In and Cd by means of a zinc amalgam: 1,2) For indium; 3,4) for cadmium (curves 2 and 4 are enlarged 25 times along the ordinate).

Elements such as As, Sb, Bi, Cu, Tl, Se, Sn, Ma, Ti, Fe(III) and some others are vigorously reduced by the zinc amalgam. Under such conditions, some (Cd, Sn, Tl, and Cu) dissolve in the mercury, while others (As, Sb, Bi, Se, and Te) are deposited in the elemental state in the form of an insoluble, friable, deposit. Elements with higher valency are reduced to lower valency states (Fe^{III}, V^{V}, Cr^{VI}, and Ti^{IV}).

The technique developed has been checked on various samples of indium raw material.

The analytical procedure adopted for the polarographic determination of indium by the amalgam method is as follows. An aliquot of test material (1-3 g) is decomposed on heating in a mixture of nitric and sulfuric acid until the sample has been broken down completely, and until copious white fumes appear. After cooling, the sample is treated with hot water, and, in the event of the presence of an appreciable amount of precipitate in the solution, the latter is allowed to stand and then filtered. To the solutions thus obtained is added sulfuric acid (or an equivalent amount of some suitable sulfate), so that its final concentration is not less than 20%; the solution is then cemented with zinc amalgam* at room temperature. The zinc amalgam is prepared by dissolving zinc metal in mercury on heating in the presence of dilute sulfuric acid. Treatment of the solution with the amalgam, for a stirrer rate of 350-400 revolutions/minute, takes about 45 minutes. When cementation is complete, the solution is filtered, if necessary, and then about 10% of its weight of a soluble chloride (for example NaCl) added to it; indium is then determined in this solution polarographically.

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*When sulfates are used it is essential to add some H_2SO_4 in order to avoid hydrolysis.

TABLE 2

Results for the Quantitative Determination of Indium in Various Types of Indium-Containing Raw Material

Firms supplying test material \ Elements in %	Bi	Zn	Al	As	Fe	Pb	Sb	Cd	Cu	Sn	Indium content as found by the following methods		
											spectro.	Aref'eva	amalgam
ChÉTsZ	0,1	20,0	10,0	0,05	0,5	0,3	0,05	0,02	0,05	0,01	5	5,00	5,01 5.00 5,00
KMZ	15,0	25,0	—	2,3	8,0	0,04	0,10	1,5	1,6	0,14	0,4	0,40	0,39 0,40 0,40
Ukrtsink	0,1	21,2	4,7	0,5	2,4	10,0	—	0,58	0,68	—	0,04	0,04	0,04 0.04 0,042

SUMMARY

A new method has been developed for removing interfering elements prior to polarographic determination of indium in concentrates and in processed materials. The method consists of treating sulfuric acid indium solutions containing 20% free sulfuric acid (or the equivalent amount of other sulfates) with a zinc amalgam; the chloride of an alkali metal is then added to the solution purified in this way, the amount of chloride added being sufficient to bring its concentration up to 10% (with respect to the weight of the solution); indium is then determined polarographically.

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INCREASING THE SENSITIVITY AND ACCURACY OF THE DETERMINATION OF CESIUM IN MINERALS BY THE FLAME-PHOTOMETRIC METHOD

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Determination of cesium in natural raw material requires highly sensitive methods, since this element is found, for the most part, in trace amounts.

The sensitivity and accuracy of the determination of cesium and other elements by flame photometry, depends not only on the refinements of the spectroscopic and electronic apparatus, but also on the techniques adopted for measurement. We have developed a flame photometric method of determining cesium, which permits hundredths and thousandths of a percent of this element to be determined in natural materials with an accuracy of 5-10%. The minimum amount of cesium (0.2 γ/ml) which can be determined by the suggested method is one and a half times that which can be determined by Horstman's method [1] which is applicable to the determination of cesium in silicates. The increased sensitivity is achieved by making use of the effect in which the intensity of the cesium radiation ($\lambda = 8521$ A) is enhanced in the presence of large amounts of potassium.

Using a flame photometric method, a study was made of the effect of the alkali elements (K, Na, Li, and Rb) present as impurities, on the intensity of the radiation of Cs at $\lambda = 8521$ A.

The test solution of cesium sulfate (0.56, 2.8, and 30γ Cs/ml) containing appropriate additions of potassium, sodium, lithium, and rubidium was introduced into an acetylene-air flame by means of a needle sprayer with a glass compartment. The spectrum line analyzer used was a UM-2 monochromator covering the spectral range 3800-10,000 A and with a linear dispersion in the red range of 335 A/mm. The radiation intensity was determined by means of a FEU-22 photomultiplier (integral sensitivity 30a/lumen) and a mirror galvanometer type M-21 (1.5×10^9 a/mm). The sensitivity was regulated by means of a 10,000 ohm resistance box connected in parallel with the galvanometer. The operating slit width of the monochromator was 0.1 mm.

During measurements of the radiation intensity of cesium, corrections were made for the background of the burner flame and the characteristic radiation of the additives.

It has been established that the presence of alkali metals in the test solution leads to an appreciable increase in the intensity of the cesium radiation ($\lambda = 8521$ A), when the concentration of the impurity is higher than the cesium concentration. Potassium shows the greatest effect. The curves relating the intensity of the Cs radiation and the potassium concentration of the solution indicate a saturation character (Fig. 1). At potassium concentrations corresponding to the saturation points, the intensity of the cesium radiation increases up to 25 times. The standard curve relating the intensity of the Cs radiation ($\lambda = 8521$ A) to cesium concentration (0.2-100 γ/ml), and taken in the presence of large amounts of potassium — 2500 γ/ml (5570 γ/ml K_2SO_4)— is almost linear; this same curve has a break when pure cesium salt is used (i.e., when no potassium is present) (Fig. 2). It is important to note then, when the test solution is "saturated" with potassium, the effect of additions of Na, Li, and also of Rb is not perceptible, as long as the amounts of these other elements are of the same order as that of cesium.

In essence, the method which has been developed reduces to the addition of large amounts of potassium sulfate (5570 γ/ ml) to both the test solution and standard solutions prior to carrying out flame-photometric measurements. The correction to be applied for the background arising from the characteristic radiation of the potassium introduced, is established by measuring the emission of a pure solution of potassium sulfate (5570 γ/ ml) when the monochromator is set at the cesium wave length (8521 A). Potassium is added to the test solution in amounts which take into account the amount of potassium already present in the original material, the original potassium content being measured with an accuracy of 50 γ /ml. The value for the original potassium contents of the test solutions are determined beforehand by flame photometric determination of potassium (λ = 7665, 7699 A) using a standard curve.

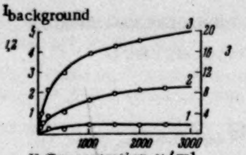

Fig. 1. Effect of potassium on the spectral emission of cesium (λ = 8521 A). Cs content: 1) 0.5 γ/ml; 2) 2.8 γ/ml; 3) 30 γ/ml; $I_{background}$, the current in scale divisions of the galvanometer.

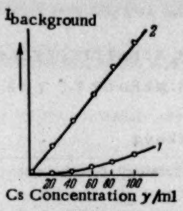

Fig. 2. Standard cesium curves. Potassium content: 1) 0; 2) 2500 γ/ ml; $I_{background}$, the current in scale divisions of the galvanometer.

Test samples are chemically prepared by Ellestad and Horstman's method [2]. The sample is broken down by means of hydrofluoric and sulfuric acids, and then precipitation carried out using basic lead carbonate. After such a treatment, the solution which is to be analyzed for cesium contains the other alkali metals (Na, K, Li, and Rb) and Mg as well as the cesium. The flame-photometric method proposed, in which potassium is added, prevents interference from the remaining impurities.

The accuracy of the method was checked by determination of cesium in a silicate sample, before and after addition of a known amount of cesium (Table 1). The mean relative error during determination of hundredths of a percent of cesium amounts to ±4.45%; during determination of thousandths of a percent of cesium the error is ±9.7%. The reproducibility of the method was checked by replicate determinations of the same amount of cesium using various calibration curves (Table 2).

Experimental procedure. 0.5-1 g of sample contained in a platinum basin is moistened with water, and 0.4 ml of concentrated H_2SO_4, 20 ml of HF, and 2-3 drops of HNO_3 added. The mixture is heated to 70-80°. As decomposition proceeds the heating is increased and is finished when white fumes appear. The residue is cooled and 2 ml of water added, this is followed by 0.1 ml of concentrated sulfuric acid and the whole heated again until white fumes appear. In order to make sure that all fluorides have been broken down, the residue is heated again after addition of 5 ml of water. 25-30 ml of water is added to the final residue and the whole heated to dissolve the salts. The liquid is transferred to a 150 ml beaker and diluted to 70 ml. The solution obtained is heated until it starts to boil gently when powdered basic lead carbonate is added to it with stirring until the liquid gives an alkaline reaction to methyl red. Solution and precipitate are boiled for several minutes, the mixture is stirred carefully and filtered through an 11 cm (white band). The precipitate is washed with hot water until the combined volume of filtrate plus washings is 120-130 ml. This solution is concentrated to a volume of 30 ml, cooled, and then filtered through a small funnel into a 50 ml standard flask; the volume is made up to the mark with water, the solution thus obtained is then the original solution to be used for the photometric measurements.

Flame-photometric measurements start with a preliminary determination of the potassium content (7665-7699 A) of this original solution, using calibration curves constructed with the aid of standard potassium solutions.

In order to determine the cesium content, an aliquot of the original solution (20 ml) is mixed in a 25 ml standard flask with a potassium sulfate solution (0.557 g / ml of K_2SO_4 or 25000 γ/ml of K) so that, after dilution of the solution to give a concentration suitable for cesium determination, it contains 2500 γ / ml of K.

TABLE 1

Determination of Cesium in Rocks

Rock	Content, in %			Cesium, in %		Relative error, in %
	Na	K	Li	added	found*	
Biotite granite	4,1	5,8	0,011	0,012	0,011	— 8,3
Vein-granite	5,4	5,8	0,007	0,029	0,031	+ 6,9
»	5,4	5,8	0,007	0,033	0,037	+12,1
Muscovite granite	3,3	5,7	0,003	0,055	0,056	+ 1.8
»	3,3	5,7	0,003	0,096	0,099	+ 3,1
Duplo-micaceous granite	3,7	5,0	0,017	0,184	0,184	0
»	3,7	5,0	0,017	0,148	0,150	+ 1,3
»	5,0	6,0	0,013	0,085	0,080	— 5,9
»	5,0	6,0	0,013	0,101	0,104	+ 3,0
Muscovite granite	3,3	6,3	0,013	0,077	0,073	— 5,2
»	3,3	6,3	0,013	0,063	0,064	+ 1.6
Duplo-micaceous granite	2,9	5,4	0,002	0,0018	0,0016	—11,1
»	2,9	5,4	0,002	0,0035	0,0032	— 8,6
»	2,9	5,4	0,002	0,0062	0,0056	— 9,6

---

*Cesium was absent in the samples of natural silicates indicated.

The volume of potassium solution to be added is calculated by means of the formula:

$$V = \frac{2500 \cdot 25 - C_K \cdot 20}{25000},$$

where C_K is the concentration of potassium in the original solution in γ/ml. Using this formula, it is possible to compile a table for the volume of potassium salt solution to add, as a function of the potassium content of the test solution, within the limits 50- 2500 γ ml.

After addition of the requisite amount of potassium, the test solution is diluted to 25 ml and this solution then used for photometric determination of cesium (λ = 8521 A). At the same time as the test solution is being measured flame-photometrically, a standard solution of cesium sulfate to which K_2SO_4 has been added in an amount corresponding to 2500 γ / ml of K, and a standard solution of potassium sulfate containing 2500 γ / ml of K, are also measured photometrically under the same conditions.

TABLE 2

Reproducibility of Cesium Determinations in the Presence of 2500 γ of Potassium /ml

Series No.	Cs found in γ/ml										Mean error, in %
1	0,17	0,17	0,19	0,20	0,15	0,21	0.16	0,17	0,20	0,18	8,8
2	2,0	1,9	2,0	1,9	1,9	2,2	1,9	2,1	2,1	2,0	4,0
3	18,2	18,3	18,1	18,2	17,4	18,5	18,3	19,1	18,7	18,4	1,5

The cesium content of the test material is calculated by means of the formula:

$$\%Cs = \frac{C_{st}\,(I_x - I_K)\; 25 \cdot 50 \cdot 100}{(I_{st} - I_K)\, Q \cdot 10^6 \cdot 20},$$

where C_{St} is the Cs concentration of the standard solution; I_{St} is the deflection of the galvanometer needle during measurement of the standard cesium solution; I_x ditto for the test solution; I_K ditto for the potassium sulfate solution; Q weight of sample in g dissolved in the original volume.

A standard solution of cesium sulfate is prepared by dissolving 1 g of CsCl in water in a 50 ml platinum basin. To this solution is added 2 ml of 4 N H_2SO_4. The contents of the basin are evaporated to dryness. The sulfate thus obtained is brought to constant weight by calcining at a weak-red heat. The salt is dissolved in distilled water in a 500 ml flask and the volume made up to the mark. The exact content of cesium in per ml of the solution obtained is calculated from the weight of the sulfate. Working solutions are prepared by dilution of this stock solution, and addition of 2500 γ/ml K. The number of working solutions depends on the range of concentrations to be measured. Thus for cesium concentrations within the range 0.2-100 γ/ml Cs we used three standards: 1 γ/ml Cs + 2500 γ/ml K; 20 γ/ml Cs + 2500 γ/ml K; and 80 γ/ml Cs + 2500 γ/ml K.

The potassium sulfate solution containing 25,000 γ/ml K was prepared from the recrystallized sulfate which had been dried at 100°. 27.85 g K_2SO_4 is dissolved in 500 ml water.

The method which has been tested out on more than 300 samples of various natural silicates, has been adopted at the Chemico-Analytical Section of the Institute of Mineralogy, Geochemistry, and Crystallochemistry of the Rare Elements, Acad. Sci. USSR.

SUMMARY

A highly sensitive method has been developed for the determination of cesium in minerals by flame photometry. This method is based on the enhanced intensity of the cesium radiation obtained on addition of large amounts of potassium to the test solution.

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SPECTROCHEMICAL DETERMINATION OF MAGNESIUM AND THE EFFECT OF THE MAGNESIUM CONTENT ON THE ANALYSIS OF SILICON AND MANGANESE IN CAST IRON

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Cast iron usually contains 0.03-0.12% of Mg; magnesium is mainly found in the form of compounds (MgS, MgO, Mg_2S, etc.) [1]. Determination of magnesium by chemical methods is fairly complicated and is not accurate enough. The use of a spectrographic method in the given instance has led to a successful solution of this problem [2-3]. Development of a technique for the determination of magnesium in cast iron, using a high-frequency spark as a spectrum-excitation source, seemed to us to be of considerable practical interest [4].

The work was carried out on a "Hilger" average dispersion spectrograph, using conditions which have been described earlier [5]. The fixed electrode used was made from copper.

A cylindrical profile with a flatly sharpened operating part 1.6 mm in diameter was chosen for sharpening the fixed electrode. This form of sharpening makes it possible, after each cleaning, to control the dimensions of the working part of the fixed electrode, and, moreover, favors treatment of the surface of the test samples by the discharge.

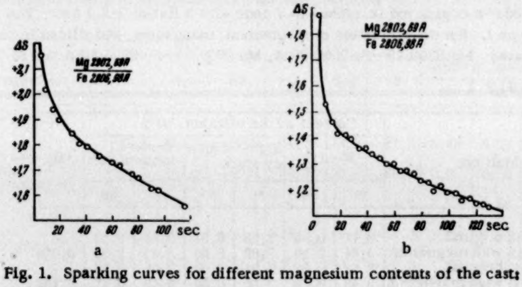

Fig. 1. Sparking curves for different magnesium contents of the cast; a) 0.12% Mg; b) 0.068% Mg.

Magnesium, which is very active chemically, interacts with individual elements, and is also readily oxidized by atmospheric oxygen. Under the action of a spark discharge incomplete burning of the magnesium from the surface layer of the sample occurs; the sparking curves testify to this (Fig. 1, a and b). Comparison of these curves, constructed for different magnesium contents of the cast, shows that after 30 seconds, there occurs some stabilization of the relative intensity of the analytical pair of lines Mg 2802.69 — Fe 2806.98 A (the slope of the lines is preserved almost the same). Accordingly, we chose a preliminary sparking time of 30 seconds. The exposure time was 20 seconds.

In Fig. 2 is shown a typical calibration curve for the determination of magnesium in cast; this curve was constructed on the basis of 15 standards prepared from production samples and carefully analyzed in several chemical laboratories.

Curves obtained with a high-frequency spark are characterized by high values for the slope. The technique suggested is distinguished by good reproducibility of the results obtained, and a completely satisfactory accuracy.

Under chosen conditions it is possible, on the basis of one photograph of the spectrum, to determine magnesium, manganese, and silicon in cast, as a result of which the time taken for determination of the element indicated in cast is considerably reduced.

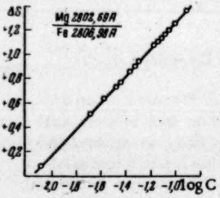

Fig. 2. Calibration curve for the determination of magnesium in cast. Spectrum excitation source—high-frequency spark.

Similar conditions were also found for a high-voltage condensed spark. The spectra were photographed under the following conditions: an IG generator, complex scheme; capacity 0.01 microfarad; induction 0.01 millihenries; analytical gap 2 mm; upper electrode—copper; sparking—60 seconds; exposure time —45 seconds. The photographic plates were spectrographic type 1.

The following pairs of analytical lines were used for the high-frequency spark method, and for the high-voltage method, for determination of magnesium, manganese, and silicon in cast;

Mg 2802.69 — Fe 2806.98 A, Mn 2933.1 — Fe 2926.6 A
and Si 2881.6 — Fe 2880.7 A.

We studied the effect of the magnesium content of the cast on the determination of silicon and manganese, using the spectrum excitation sources indicated. Table 1 contains results obtained during the analysis of silicon and manganese in cast before and after addition of magnesium. As these results show, the magnesium content has no effect on the results of the spectrochemical determination of silicon and manganese.

For studying the effect of the magnesium content on the analytical results for silicon and manganese in cast, by means of an a.c. arc, production samples were used. The spectra were photographed on an ISP-22 spectrograph under the following conditions: spectrum excitation source— an a.c. arc PS-39, current 4 amps; analytical gap 2 mm; slit width of the spectrograph—0.015 mm; arcing —10 seconds; exposure time —15 seconds; upper electrode—a copper rod sharpened to a cone with a flat of 2-2.5 mm. The photographic plates were spectrographic type 1. For determination of magnesium, manganese, and silicon in cast, the following analytical lines were used: Mg 2802.69—Fe 2806.98 A, Mn 2939.30—Fe 2926.59 A and Si 2519.21—Fe 2518.10 A.

TABLE 1

Melt no.	Content of the element, in %						Mg
	IG-2		high-frequency spark		chemical composition		
	Si	Mn	Si	Mn	Si	Mn	
313 original	3,71	0,56	3,65	0,57	3,67	0,55	—
313 with magnesium	3,64	0,56	3,66	0,56	3,64	0,53	0,098
400 original	3,52	0,58	3,54	0,60	3,55	0,59	—
400 wigh magnesium	3,48	0,59	3,50	0,58	3,49	0,57	0,108
400 original	3,64	0,61	3.61	0,62	3,62	0,63	—
403 with magnesium	3,55	0,63	3,59	0,59	3,57	0,60	0,098
418 original	3,73	0,69	3,70	0,68	3,75	0,70	—
418 with magnesium	3,69	0,68	3,71	0,67	3,71	0,69	0,162

In order to study the effect of magnesium on the relative intensities of the lines for silicon and manganese in cast, sparking curves were constructed for these elements (Fig. 3, a,b). A comparison of these curves shows that the relative intensity of the silicon and manganese lines increases appreciably for casts with high magnesium contents as compared with the original casts (for the same amounts of silicon and manganese in these casts). Casts with different magnesium contents were examined (Table 2).

The results obtained make it possible to assess the difference in the effect of magnesium on the absolute and relative intensity of the silicon and manganese lines; it is dependent, in the first instance, on the amount of magnesium in the cast iron.

For magnesium contents in the cast up to 0.04%, the absolute intensities of the silicon and manganese lines, and of the comparison lines are somewhat lower than the absolute intensities of the lines of these same elements in the original cast. But, since the corresponding relative intensities of the test lines of the magnesium cast and the original cast are very similar in value, the effect of magnesium of the final analytical results is almost excluded.

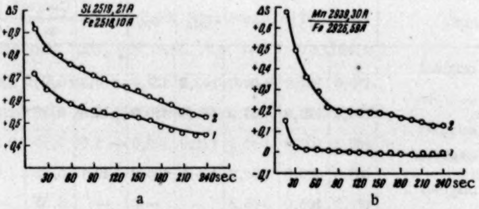

Fig. 3. Sparking curves for silicon (a) and manganese (b); 1) Original cast; 2) cast to which magnesium has been added (0.12% Mg) Spectrum excitation source—a PS-39 arc generator.

It is evident from Table 2 that for magnesium contents, for example, of 0.011%, the results for silicon and manganese in the original and in the magnesium cast, are almost identical and correspond to the true values; this was confirmed by chemical analysis.

At higher magnesium contents of the cast—up to 0.06%— the absolute and relative intensities of the silicon and manganese lines are somewhat higher than one would expect.

TABLE 2

Sample	S_{Si}	S_{Fe}	ΔS	S_{Mn}	S_{Fe}	ΔS	Content, in %		
							Si	Mn	Mg
Melt 299 – original cast	64,0	113,2	−49,2	64,7	132,0	−67,3	0,60	0,27	—
Melt 299 – cast plus magnesium	61,9	111,2	−49,3	60,7	130,0	−69,3	0,60	0,26	0,011
Melt 406 – original cast	169,8	109,1	+60,7	124,0	119,5	+ 4,5	3,51	0,66	—
Melt 406 – cast plus magnesium	167,1	106,7	+60,4	119,5	115,2	+ 4,2	3,48	0,65	0,024
Melt 427 – original cast	121,1	89,8	+31,3	110,0	100,0	+10,0	1,70	0,72	—
Melt 427 – cast plus magnesium	120,5	88,9	+31,6	109,5	100,0	+ 9,5	1,73	0,71	0,033
Melt 303 – original cast	117,9	80,0	+37,9	75,3	101,0	−25,7	2,02	0,36	—
Melt 303 – cast plus magnesium	120,1	76,4	+43,7	81,5	97,5	−16,0	2,37	0,43	0,045

The effect of the magnesium content of the cast on the intensity of the silicon and manganese lines is most clearly demonstrated at magnesium contents higher than 0.06% (Table 3).

The results given in Table 3 show that the relative intensity of the lines in samples of the original cast and in cast containing magnesium, with approximately equal amounts of silicon and manganese, differs essentially. The intensity of the silicon and manganese lines in cast containing magnesium is appreciably higher than that of the lines in the original cast; this is a consequence of the effect of magnesium. Results for the spectrographic determination of silicon and manganese in magnesium cast are one and a half to twice the true content of these elements in the metal.

Many examples are given in the literature of the effect of the third component on the results of the determinations of a number of elements [6, 7, 8].

On the basis of the experiments described above it is clear that with increasing magnesium content, which affects the fusion temperature of the melt, the intensity of the analytical lines of silicon and manganese increases when an arc discharge is used. This leads to the conclusion that magnesium affects the evaporation process of these elements in the arc, and, consequently, affects the experimental results. Similar phenomena have been observed during the analysis of copper alloys, [9], and, to a smaller extent, during the analysis of aluminum alloys [10].

TABLE 3

Sample	S_{Si}	S_{Fe}	ΔS	S_{Mn}	S_{Fe}	ΔS	Content, in %		
							Si	Mn	Mg
Melt 312 – original cast	170,0	104,0	+66,0	132,8	127,0	+ 5,8	3,94	0,62	—
Melt 312 – cast plus magnesium	180,0	93,0	+84,0	146,8	110,0	+46,8	6,38	1,22	0,118
Melt 313 – original cast	169,3	105,0	+64,3	121,0	122,0	— 1,0	3,76	0,55	—
Melt 313 – cast plus magnesium	183,0	103,0	+80,0	145,1	105,0	+40,1	5,75	1,09	0,098
Melt 409 – original cast	171,3	105,0	+66,3	—	—	—	3,55	—	—
Melt 409 – cast plus magnesium	180,0	95,0	+85,0	—	—	—	5,62	—	0,068
Melt 400 – original cast	172,0	110,8	+61,2	154,0	150,5	+ 3,5	3,55	0,62	—
Melt 400 – cast plus magnesium	187,0	105,0	+82,0	176,0	129,0	+47,0	6,69	1,17	0,108
Melt 403 – original cast	172,0	110,0	+62,0	152,0	147,0	+ 5,0	3,63	0,64	—
Melt 403 – cast plus magnesium	185,0	102,5	+82,5	185,0	134,0	+51,0	5,75	1,29	0,098
Melt 418 – original cast	162,0	102,0	+60,9	114,5	110,0	+ 4,5	3,76	0,73	—
Melt 418 – cast plus magnesium	172,0	98,0	+74,0	138,0	100,0	+38,0	5,50	1,12	0,163
Melt 420 – original cast	167,1	102,0	+65,1	135,0	131,0	+ 4,0	3,89	0,60	—
Melt 420 – cast plus magnesium	176,5	93,0	+83,5	154,0	108,0	+46,0	6,31	1,12	0,160

SUMMARY

1. A technique has been developed for the spectrographic determination of magnesium in modified cast iron using a high-frequency spark as a spectrum excitation source. The technique permits determination of 0.005%, and more, of magnesium.

2. It has been established that the intensity of the spectral lines of silicon and manganese in cast depends to a considerable extent on the magnesium content of the cast when an arc discharge is used. The intensity of the lines of these elements increases appreciably with increasing magnesium content. For magnesium contents of the cast in excess of 0.06%, the amount of the silicon and manganese as determined spectrographically is one and a half to a twice as much as the true content of these elements in the metal.

3. Magnesium does not affect the results obtained during spectrographic determination of Si and Mn in casts, when a condensed spark generator and a high-frequency spark are used.

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PHOTOMETRIC DETERMINATION OF TOTAL RARE EARTHS IN ORES AND ROCKS

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Tha aim of our investigation was to develop a photometric method for determining from 0.01 to 2-3% of total rare earths (T.R.E) in ores and rocks. The work is a continuation of work published earlier [1, 2] on the use of arsenazo I [3] and the method of developing reagents [2].

The chlorides of the rare earths of the cerium (T.R.E. -Ce) and yttrium groups (T.R.E. -Y) were used in this work. Total rare earths were extracted from the minerals by the usual oxalate method. Their chemical composition was (in %): T.R.E. -Ce — Ce_2O_3 41.0; La_2O_3 13.3; Pr_2O_3 5.5; Nd_2O_3 23.0; Sm_2O_3 5.0, etc., T.R.E. - Y(Y_2O_3, Er_2O_3) 58.0. etc.

1% Solutions of the chlorides of the T.R.E. and the content of the T.R.E. in these solutions was established gravimetrically after precipitation with ammonia. The working solution was prepared from the 1% solution of T.R.E. containing 30γ T.R.E./ml and had a pH of 3.

TABLE 1

Optical Density of Solutions of the Complexes of the Metals with Arsenazo in the Presence (I), and in the Absence (II) of Sulfosalicylic Acid

Metal oxide, 30γ/25 ml	Optical density		Equivalent to T.R.E.		Difference in γ of T.R.E.	
	(I)	(II)	(I)	(II)	(I)	(II)
T.R.E. - Ce	0,21	0,20	30,0	30,0	—	—
T.R.E. - Y	0,22	0,21	30,0	30,0	—	—
Y_2O_3	0,30	0,32	42,0	48,5	+12,0	+18,5
Ce_2O_3	0,24	0,22	32,5	31,0	+ 2,5	+ 1,0
La_2O_3	0,20	0,22	28,5	35,0	— 1,5	+ 5,0
ThO_2	0,18	0,09	25,0	14,0	— 5,0	—16,0
ZrO_2	0,01	0,01	1,5	1,5	—28,5	—28,5
TiO_2	0,02	0,06	2,5	8,0	—27,5	—22,0
Al_2O_3	0,00	0,27	0,00	41,0	0,00	+11,0

The solutions used for studying the optical properties of the complexes of the metals with arsenazo were prepared as follows. Into a 25 ml standard flask was introduced a solution containing the metal ion (equivalent to 30 γ of the metal oxide), 0.5 ml of 10% sulfosalicylic acid, 3 ml of 0.05% arsenazo solution, and 4 ml of a 20% solution of urotropine, and the whole made up to the mark with water and mixed; the pH of such a solution was 6.7-6.8. The reference solution was prepared in the same way but with omission of the metal salt.

The optical density of the solutions (Table 1) was measured on a FEK-M photocolorimeter, using 30 mm cells and a yellow-green filter (λ 570 mμ).

Equimolar amounts of the elements of the cerium and yttrium groups give solutions with almost equal optical density with arsenazo. Increasing the yttrium content of the T.R.E. will increase the optical density since yttrium taken individually increases the optical density in comparison with cerium and lanthanum. As can be seen from Table 1, in the presence of sulfosalicylic acid, titanium (IV) and zirconium have almost no effect on the optical density, while thorium increases it.

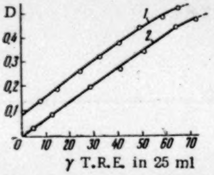

Fig. 1. Optical density of the complexes of the rare earths with arsenazo in the presence of 1.5 mg of calcium (Curve 1) and in the absence of calcium (Curve 2).

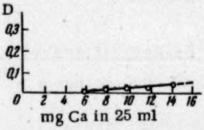

Fig. 2. Optical density of the complex of calcium with arsenazo in the presence of 50 mg sulfosalicylic acid.

In neutral media, calcium forms a complex with blue-violet color with arsenazo. Calcium is often met in large quantities in ores, and is also used as a precipitant in the oxalate method. In Fig. 1, is shown the optical density of the complexes of the T.R.E. with arsenazo in the presence of 1.5 mg of calcium (Curve 1), and in the absence of calcium (Curve 2). Calcium sulfosalicylate is colorless, it does not give a color with arsenazo. In Fig. 2, is shown the optical density of the complex of calcium with arsenazo in the presence of 50 mg of sulfosalicylic acid per 25 ml solution. In the presence of sulfosalicylic acid, as can be seen from Fig. 2, no color resulting from the complex develops at calcium contents up to 6 mg; greater amounts of calcium increase the optical density of the solution significantly.

Separation of thorium from the rare earths. Thoron [4], arsenazo [3], pyrocatechol violet [5], hydroxyhydroquinone rose [6], quinalizarin [7], and Schiff Base,* and many other compounds form finely dispersed deposits, in the form of a suspension, with thorium. Separation of the suspension from the aqueous phase by the use of fine-pore filters is not possible, but activated charcoal readily adsorbs the thorium complex and also the reagent.

To 30 ml of solution containing 218 γ thorium and 215 γ T.R.E., at the pH shown in Table 2 to be the optimum for color development, was added 2 ml of a 0.1% aqueous (alcoholic for quinalizarin and the Schiff Base) solution of the reagent in a large excess. On mixing, a color characteristic of the given complex developed. After 2-3 minutes, 0.1 g of activated charcoal was added to the solution and the whole shaken up, and then filtered through a "white band" filter 9 cm in diameter.

Thorium was determined in the solution and in the adsorbent (after burning off the carbon) by a method described in one of our papers [1], while the T.R.E. was determined as described above.

It is clear from Table 2 that pyrocatechol violet, hydroxyhydroquinone rose, and quinalizarin do not permit separation of thorium and T.R.E. since the T.R.E. are adsorbed from the solution as well as thorium. Using thoron, arsenazo, and the Schiff Base, it is possible to separate thorium and T.R.E.

When the Schiff Base is used, thorium can be quantitatively separated from T.R.E. in one operation. Thoron ** gives satisfactory results.

It is, however, more expedient to use the Schiff Base since this can be readily prepared in the laboratory. Using thoron, it is possible to separate up to 148 γ of thorium (Table 2) in one adsorption.

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*Prepared from salicaldehyde and o-aminoarsonic acid.

**Issued by Russian industry.

TABLE 2

Separation of Thorium from T.R.E. in the Form of Different Complex Compounds by Means of Activated Charcoal (in 30 ml solution with 218 γ Th and 215 γ of T.R.E.)

Reagent	Optimum acidity for color development	Distribution, in γ			
		charcoal		solution	
		Th^{4+}	T.R.E.	Th^{4+}	T.R.E.
Thoron	0,05—0,1 *N*	148	—	55	210
Arsenazo	0,05—0,1 *N*	80	—	130	200
Pyrocatechol violet	pH 2,4—3	220	122	—	110
Hydroxyhydroquinone rose	pH 2,4—3	208	160	—	50
Quinalizarin	pH 3—4	220	180	—	20
Schiff Base	0,05—0,1 *N*	208	—	—	220

Zirconium behaves like thorium.

Separation of the rare earths from accompanying metals by the method of "in situ nascendi" reagents.

The method of "in situ nascendi" reagents was also used for separating T.R.E. from accompanying metals. The oxalate ion which is formed during the hydrolysis of acetonedioxalic acid gives coarse-crystalline precipitates of the oxalates of the rare earths [2].

To 100 ml of a hydrochloric acid solution (pH about 5) containing T.R.E., thorium, iron, titanium, and zirconium in the amounts indicated in Table 3, was added 0.5 ml of a 25% solution of calcium chloride (25 mg calcium) and 15 ml of a solution of acetonedicarboxylic acid corresponding to about 4 g of oxalate ions. The solution was boiled on a closed asbestos electric hot plate for 15 minutes; on the second day after mixing, the precipitate was filtered through a double "white band" filter 9 cm in diameter, and washed 4-5 times with a 1% solution of oxalic acid. The precipitate was transferred to a porcelain crucible and calcined at 700°. The residue obtained was transferred to a 100 ml beaker, moistened with water, and 3-4 ml of hydrochloric acid sp. gr. 1.19 added. The acid was evaporated until a moist residue of salts was obtained: the chlorides of T.R.E., thorium, and calcium were dissolved in 30 ml of water and the acid neutralized with 10% ammonia solution using congo-red paper as indicator (pH about 4), 0.5 ml of hydrochloric acid sp. gr. 1.12 was then added, followed by 2 ml of a 0.1% solution of thoron, and, after mixing, 0.1 g of activated wood charcoal added. The solution was mixed for 20-25 seconds and filtered through a "white band" filter, 9 cm in diameter. This operation was repeated. After removal of thorium (and traces of zirconium) from the T.R.E., ammonia solution was added until the pH was 4 (blue-violet color of congo paper), and the solution transferred to a 50 ml standard flask; the volume was made up to the mark with water and T.R.E. determined. For this purpose equal aliquot parts of the solution obtained — from 2 to 10 ml — were transferred to two 25 ml standard flasks.

One of these solutions was used as a reference solution, while the other was used for colorimetric measurements. To the reference solution was added 0.5 ml of a 1% solution of ascorbic acid, 0.35 ml of 10% tartaric acid, 3 ml of a 0.05% arsenazo solution, and 4 ml of 20% urotropine solution; the volume was then made up to the mark with water and mixed. To the solution to be used for colorimetric measurements was added 0.5 ml of 1% ascorbic acid, 0.5 ml of 10% sulfosalicylic acid, 3 ml of 0.05% arsenazo solution, and 4 ml of 20% urotropine solution; the volume was made up to the mark with water, the whole was thoroughly mixed and colorimetric measurements made after 30 minutes.

A calibration curve was constructed as follows: into 14 standard flasks of 25 ml capacity were introduced various amounts of a standard solution of the T.R.E. containing 5-10-15....70 γ T.R.E., calcium chloride solution equivalent to 5 mg of calcium was added to each flask, followed by 0.5 ml of 10% sulfosalicylic acid, 3 ml of 0.05% arsenazo solution, and 4 ml of 20% urotropine solution. The solutions were mixed and the optical density measured after 30 minutes as indicated above. The reference solution was prepared in the same way, but with omission of the T.R.E.

Completely satisfactory results were obtained (Table 3).

TABLE 3

Separation of T.R.E. from Accompanying Elements

Taken					T.R.E. found, in γ	Error in T.R.E., in γ
Fe^{3+}, mg	Ti^{4+}, mg	Zr^{4+}, mg	Th^{4+} γ	T.R.E., in γ		
50,0	5,0	5,0	268,0	50,0	56,0	+ 6,0
50,0	5,0	5,0	175,7	84,0	97,5	+13,5
50,0	5,0	5,0	200,0	127,2	125,0	— 2,2
50,0	5,0	5,0	200,0	169,6	160,0	— 9,6
50,0	5,0	5,0	200,0	254,4	245,0	— 9,4
50,0	10,0	10,0	200,0	212,0	215,0	+ 3,0
50,0	10,0	10,0	200,0	212,0	215,0	+ 3,0
50,0	5,0	5,0	200,0	127.2 T.R.E. +118,0 Y_2O_3 245,2	255,0	+ 9,8

Determination of total rare earths in materials with a complex composition. 1 g of dry sodium peroxide was placed in a 10 ml porcelain crucible; this was followed by 0.0250-0.2500 g of sample and a further 3-4 g of sodium peroxide. The crucible was placed inside a large crucible and transferred to a muffle furnace heated to 300°. The temperature was taken up to 550° and fusion carried out until a homogenous melt was obtained. The cooled melt was dissolved in 100 ml of water on heating in the course of 20-25 minutes. After cooling, the crucible was taken out of the beaker and the solution filtered through a 9 cm "white band" filter; the hydroxides on the filter paper were washed 2-3 times with water and dissolved in 20-30 ml of 5% (by volume) hot hydrochloric acid, a saturated solution of sodium acetate was then added dropwise until the pH was 5 (congo-red paper), the volume of the solution was made up to 100 ml and the procedure outlined above subsequently followed.

TABLE 4

Photometric Determination of T.R.E. in Synthetic Mixtures

Main components	Sample wt., in g	T.R.E. content, in %	T.R.E. found, in %	Error, in %
SiO_2 50,0; Fe_2O_3 3,0	0,1565	0,21	0,21	
Al_2O_3 12,0; CaO 12,0	0,1182		0,22	+9,5
ThO_2 0,1	0,0886		0,26	
Ditto + 5,0 ZrO_2 +10,0 TiO_2	0,0800	0,21	0,22	+4,8
Ditto	0,0820	2,0	1,95	—2,5
Ditto	0,0310	2,0	1,97	—1,5

The results (Table 4 and 5) proved to be completely satisfactory, although considerable deviations were obtained sometimes (+ 27.0 and + 49%). This is a consequence of the fact that the gravimetric method is not accurate enough.

Normal contents of up to 40% yttrium in ores and rocks may be 5-6% higher than the actual amount when this method is employed, but this is quite permissible.

TABLE 5

Determination of T.R.E. in Ores and Rocks

T.R.E. content, in %		T.R.E. found photometrically, in %		Error, in %
determined gravimetrically	T.R.E. added	with addition of T.R.E.	without addition of T.R.E.	
2,27	—	—	2,20	+3,0
0,97	—	—	1,07 0,90	+ 1,6
0,13	0,10	0,25	0,14	+ 7,0
0,11	0,10	0,25	0,14	+27,0
0,23	0,10	0,35	0,25	+ 9,0
0,08	0,10	0,18	0,07	−14,0
0,21	—	—	0,17 0,19	−16,6
0,047	—	—	0,07	+49,0
0,39	—	—	0,38 0,40 0,43	+ 3,3
0,06	—	—	0,06 0,07	+ 8,3

SUMMARY

It has been established that solutions of the complexes of the rare earths of the cerium and yttrium groups with arsenazo conform to Beer's law. Interference from calcium and other elements during photometric determinations can be prevented by means of sulfosalicylic and tartaric acids.

A method is suggested for separating small amounts of thorium from total rare earths.

A photometric method has been developed for the determination of 0.01 to 3% of total rare earths in ores and rocks with an experimental error of 5-20%. It takes 8-10 hours to carry out 8-10 analyses.

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GRAVIMETRIC AND PHOTOMETRIC DETERMINATION OF THE THORIUM CONTENT OF URANINITES BY MEANS OF ANTHRANILIC ACID

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Organic reagents have found wide application in recent years for the separation of thorium during the analysis of natural materials. Phenylacetic, anthranilic, phenylpropionic [1], naphthylacetic [2], o-chlorophenoxyacetic [3], acetylsalicylic, and guaiacolacetic acids [4] permit separation of thorium from the rare earths, but not from uranium. Thorium can be separated from uranium by means of ferron [1], and naphthionic and sebacic acids, etc [5, 6]. Meta-nitrobenzoic acid [1], o-chlorobenzoic and 2,4-dichlorophenoxyacetic acids have been suggested for the separation of thorium from uranium and the rare earths in each other's presence.

Most of the reagents listed have only been used by the authors for the separation of appreciable amounts of thorium. For isolating small amounts of thorium (less than 1 mg) only phenylacetic, phenylpropionic, and naphthyl acids have been used.

Natural uraninites, in addition to their high uranium content, and the presence of lead and the rare earths in them, contain relatively small amounts of thorium. It was of interest therefore to select a method for determining thorium, which would allow one to separate thorium easily, and finally determine the amount of thorium present. For this purpose we chose anthranilic acid.

Isolation of thorium from solutions by means of anthranilic acid. Anthranilic acid has not been used for isolating small amounts of thorium. An idea of the possibility of precipitating large amounts of thorium by means of this reagent can be gained from the work of Murthy and Rao [7].

We precipitated thorium as follows. To a thorium nitrate solution heated to the boiling point was added 0.5 g of ammonium acetate and various amounts of a 0.35% aqueous solution of anthranilic acid; after boiling for two minutes, the precipitate was filtered off, washed a few times with hot water and then calcined to ThO_2. The volume did not exceed 50 ml in any of the experiments.

It follows from the results given in Table 1, that under certain conditions, thorium can be quantitatively precipitated by means of anthranilic acid; a large excess of precipitant does not interfere with complete separation.

In order to establish the optimum acidity for carrying out the precipitation, thorium was precipitated with anthranilic acid at various pH values of the solution; the pH was regulated by an acetate buffer mixture.

Quantitative deposition of thorium anthranilate was found to occur in the pH range 4.2 to 5.6 (Table 2). Further increases in the pH of the solution led to partial dissolution of thorium anthranilate.

Precipitation of thorium in the presence of uranium. It was established that it is best to precipitate thorium in the presence of uranium at a pH of 4.2-4.4; nevertheless, under these conditions, up to 30% of the uranium is coprecipitated with the thorium. In order to keep uranium in solution we complexed it with hydroxylamine hydrochloride. The addition of hydroxylamine to the solution does not prevent precipitation of thorium by anthranilic acid.

In order to establish what are the maximum amounts of uranium in whose presence thorium can still be precipitated with anthranilic acid, various amounts of uranyl nitrate were added to solutions containing 3 mg ThO_2 so that the ratio of $ThO_2 : U_3O_8$ in the final solutions amounted to 1 : 10, 1 : 15, 1 : 50, and 1 : 100. 1 g of hydroxylamine hydrochloride and 0.5 g of ammonium acetate was added to each solution, and a dilute ammonia solution free from CO_2 used for adjusting the pH of the solution to the required value, methyl orange being used as indicator. The solution was then heated and thorium precipitated with 10 ml of a 0.35% solution of anthranilic acid. After being allowed to stand for 15 minutes, the precipitate was filtered, washed with hot water, and then calcined to ThO_2. In order to ensure more complete removal from uranium, the precipitate was reprecipitated. For this purpose the precipitate of thorium anthranilate was dissolved in dilute 1 : 5 nitric acid, the latter being added dropwise, 1 g of hydroxylamine hydrochloride was added and the pH controlled as during the first precipitation; thorium was then precipitated again with 0.35% reagent solution.

TABLE 1

(6.0 mg ThO_2 taken)

Amount of anthranilic acid, in mg	ThO_2 found, in mg	Error, in mg
3.5	5.2	−0.8
7.0	5.2	−0.8
14.0	5.8	−0.2
20.0	6.0	-0
35.0	6.1	+0.1
52.0	6.0	0
70.0	6.1	+0.1

TABLE 2

(6.0 mg ThO_2 taken)

pH	ThO_2 found, in mg	Error, in mg	pH	ThO_2 found, in mg	Error, in mg
3.7	0	−0.6	5.0	5.9	−0.1
4.0	5.6	−0.4	5.2	6.1	+0.1
4.3	5.9	−0.1	5.4	5.9	−0.1
4.5	6.0	0	5.6	5.9	−0.1
4.6	6.1	+0.1	6.0	4.8	−1.2
4.8	6.0	0	6.2	4.6	−1.4

TABLE 3

(3.0 mg ThO_2 taken)

U_3O_8 taken, in mg	ThO_2 found, in mg	Error, in mg
30.0	3.10	+0.1
50.0	3.15	+0.15
150.0	3.20	+0.2
300.0	3.30	+0.3

TABLE 4

(8.0 mg ThO_2 taken)

CeO_2 taken, in mg	ThO_2 found, in mg	Error, in mg
6.0	8.0	0
12.0	8.0	0
18.0	8.0	0
24.0	8.1	+0.1
36.0	8.1	+0.1
66.0	8.2	+0.2
128.0	8.7	+0.7

It follows from the results given in Table 3, that by complexing sexivalent uranium with hydroxylamine, it is possible to separate fairly small amounts of thorium from uranium in amounts which are considerably in excess of that of the thorium.

Similar experiments were carried out on the separation of thorium by means of anthranilic acid in the presence of the rare earths and lead (Tables 4 and 5).

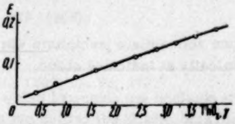
According to these results, up to ratios of $ThO_2 : CeO_2$ = 1 : 8, thorium is almost completely separated from the rare earths by means of anthranilic acid. Lead, as the results given in Table 5 show, is not precipitated by means of anthranilic acid under the experiments conditions used.

Photometric determination of thorium. According to Murthy and Rao's results [7] the salt formed between thorium and anthranilic acid has a definite composition which corresponds to the formula $[(C_7H_6O_2N)_2(ThOH)_2]$. On the other hand, it is known that during diazotization of anthranilic acid and subsequent treatment with β-naphthol there is formed an orange dye [8]. The dye formed is azo-β-naphtho-β-benzoic acid. We thought it would be of interest therefore to use the colored compound obtained by diazotization for the photometric determination of the thorium anthranilate isolated. This would permit the limits of applicability of this method to be extended considerably.

TABLE 5

(5.0 mg ThO_2 taken)

PbO taken, in mg	ThO_2 found, in mg	Error, in mg
10.0	5.1	+0.1
20.0	5.2	+0.2
40.0	5.1	+0.1
50.0	5.2	+0.2
60.0	5.2	+0.2
75.0	5.3	+0.3



Calibration curve for the determination of thorium.

Conditions for obtaining the colored compound were chosen first. Diazotization was carried out in hydrochloric acid solution with cooling. For this operation we used a 4% solution of sodium nitrate and a 1% solution of β-naphthol in 5% sodium hydroxide. The optimum amounts of the reagents participating in the reaction are: 1 ml of NaOH and 1 ml of β-naphthol in 50 ml of solution. At a pH of 1.6-2.6 for the original solution, a bright-orange precipitate of the azo dye separated out; the dye was insoluble in alkali. At a pH of 2.9-4.0 transparent brightly colored solutions of the dye were obtained. At a pH of 5 and higher the solutions did not become colored on addition of β-naphthol.

The color shade of the dye can change from yellow orange to lemon yellow depending on the pH of the solution.

The most suitable shade for photometric measurements proved to be the yellow-orange shade obtained at a pH of 2.9-4.0. The absorption maxima for the dye lie at 280 and 340 mμ. The optical density of the colored solution remains constant over several days. When pure anthranilic acid was used, it was found that there was a linear relation between the color of the dye formed by diazotization and the concentration of anthranilic acid.

TABLE 6

ThO_2 taken, in mg	ThO_2 found, in mg	Error, in mg
0.50	0.525	5.0
0.50	0.520	4.0
0.36	0.360	0
0.30	0.310	3.3
0.30	0.290	3.3
0.20	0.190	5.0

For determination of thorium in solution containing from 0.2 to 0.5 g of ThO_2 in the form of the nitrate, precipitation with anthranilic acid was carried out as indicated above. The precipitated thorium anthranilate was carefully washed with hot water and alcohol for removing excess free anthranilic acid. The precipitate was then dissolved in 25 ml of 0.1 N HCl and the solution transferred to a 50 ml standard flask, and the volume made up to the mark with distilled water. Aliquots which were taken from this solution (10-20 ml, depending on the intensity of the color of the dye formed) were cooled, and 1 ml of 4% $NaNO_2$ and 1 ml of 1% β-naphthol solution added. The solutions were diluted to a volume of 50 ml in standard flasks and the color measured in 10 ml cells, using a blue filter; distilled water was used as the reference solution. The ThO_2 content was established by means of a calibration curve.

As the results given in Table 6 shows, the experimental error of the method amounts to 3-5%.

Determination of thorium in uraninite by means of anthranilic acid. We adopted the following method for isolating and determining thorium during the analysis of uraninites: 25-400 mg of the uraninite was dissolved in 10 ml of HNO_3 (1 : 5). The solution was heated until nitrogen oxide fumes were liberated, 20 ml of water was added, followed by 1-2 g of hydroxylamine hydrochloride; the pH of the solution was then adjusted by addition of 0.5 g of ammonium acetate and dilute 1% ammonia solution, using methyl orange as indicator.

The solution was heated to the boiling point and thorium precipitated with 20 ml of a 0.35% aqueous solution of anthranilic acid. After standing for 15 minutes, the precipitated thorium anthranilate was filtered off, washed with hot water, and then reprecipitated. The latter was carried out by washing the precipitate off the filter with 25 ml of dilute HCl (1 : 10) into a beaker; 1 g of hydroxylamine hydrochloride was added again, the pH was adjusted to about 4.5, and the thorium precipitated again with anthranilic acid as indicated above.

The thorium anthranilate precipitate was calcined and then weighed as ThO_2, or the thorium was determined photometrically as indicated above.

The results obtained are compared below in Table 7 with those obtained by precipitation of thorium with phenylacetic acid, which was carried out during the systematic analysis of uraninite.

TABLE 7

Uraninite sample no.	Sample weight, in mg	ThO_2, as found by the anthranilic acid method			ThO_2, as found by the phenylacetic acid method
		in mg	in %	mean value	
1*	356,7	9,5	2,63	2,58	2,60
	138,2	3,7	2,69		
	138,0	3,5	2,46		
	123,9	2,2	2,58		
2*	295,0	7,1	2,40	2,36	2,30
	335,0	7,9	2,36		
	287,8	6,8	2,37		
	443,9	10,3	2,34		
3**	26,8	0,44	1,64	1,65	1,60
	46,8	0,76	1,60		
	46,6	0,80	1,73		
3**	37,5	0,83	2,21	2,23	2,24
	24,8	0,66	2,26		

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*Gravimetric determination.

**Photometric determination.

The method suggested for the isolation of thorium in the form of its anthranilate, and its subsequent photometric determination after diazotization of the anthranilate, gives results which are in good agreement with the longer analytical methods.

SUMMARY

1. A study has been made of the possibility of separating thorium in the presence of uranium, the rare earths and lead, by means of anthranilic acid. It has been shown that thorium can be quantitatively precipitated at concentrations not less than 0.2 mg/50 ml.

2. A photometric method for determining thorium is suggested, which is based on formation of a colored compound as a result of the reaction between anthranilic acid, nitrous acid, and β-naphthol. The method is highly sensitive, and permits determination of down to 0.04 γ of Th/ml. The method of isolating and determining thorium has been applied to the analysis of natural uraninites, and has given completely satisfactory results.

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KINETIC METHODS OF QUANTITATIVE ANALYSIS. COMMUNICATION 5.

A KINETIC METHOD FOR THE DETERMINATION OF TANTALUM

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In previous articles [1, 2] we have dealt with kinetic methods of determining molybdenum and tungsten, which were based on the catalysis of the oxidation of iodide by hydrogen peroxide in an acid medium. In the work described here the catalysis of this reaction by Ta(V) compounds was used for developing a kinetic method for the quantitative determination of low concentrations of tantalum.

The working solutions were 0.01 M solutions of KI and H_2O_2, a 1 M solution of HCl, and a 0.2% starch solution. All the reagents were given special purification to free them from heavy metals.

The tantalum solution was prepared by fusing an aliquot of Ta_2O_5 with potassium pyrosulfate and leaching the melt with a saturated solution of ammonium oxalate. The tantalum content of the solution was established by means of the tannin method.

The theoretical principles of kinetic methods of chemical quantitative analysis have been discussed in detail previously [3].

The following technique was used. Into a 50 ml standard flask was introduced the solution of tantalum, followed by potassium iodide and starch, and the volume made up to a volume of 40-43 ml and then thoroughly mixed. To this solution was then added the requisite amount of hydrogen peroxide, and the volume made up to the mark with water, the whole was mixed again and finally introduced into the cell of a FEK-M photocolorimeter. At the moment the hydrogen peroxide was added to the solution a stop watch was started, and the optical density then measured at equal time intervals. The initial concentrations of the reactant were as follows: tantalum, from 2×10^{-6} to 5×10^{-5} M; potassium iodide, from 2×10^{-4} to 2×10^{-3} M; hydrogen peroxide, from 2×10^{-4} to 2×10^{-3}; and hydrochloric acid, from 0.1 to 0.5 M.

The optical density of the solution is proportional to the concentration of the liberated iodide, while the change of optical density in unit time is proportional to the rate of reaction. The over-all equation of the reaction is:

$$H_2O_2 + 2I^- + 2H^+ \rightleftarrows I_2 + 2H_2O. \qquad (1)$$

In order to establish the form of the equation of the reaction rate, a study was made of the relation between the reaction rate and the concentration of the individual reagents. The results obtained are shown graphically in Figs. 1-4. On the basis of an analysis of the results obtained, the equation for the rate of reaction can be written as follows:

$$d[I_2]/d\tau = (\varkappa_0 + \varkappa_1 C_{H^+}) \cdot C_{I^-} \; C_{H_2O_2} \cdot C_{Ta}, \qquad (2)$$

where C_I, $C_{H_2O_2}$, C_{H^+}, and C_{Ta} are the concentrations of iodide, hydrogen peroxide, acid, and catalyst (Ta), respectively, κ is the catalytic coefficient (reaction rate constant). The curve relating the reaction rate and hydrogen ion concentration does not pass through the origin; this can be explained on the grounds that the reaction proceeds in two direction [4].

The curve relating reaction rate and tantalum concentration (the concentrations of the other reagents being constant) is, in essence, a calibration curve for the determination of Ta.

The effect of foreign ions on the accuracy of tantalum determination by the given method was studied.

Effect of Foreign Ions

Ion	Conc. of foreign ion, in mole/liter	Ratio of conc.	Tangent α, min^{-1} · 10^2	Relative error	Ion	Conc. of foreign ion in mole/liter	Ratio of conc.	Tangent α, min^{-1} · 10^2	Relative error
K^+	10^{-2}	1:1000	0,33	—3	F^-	10^{-3}	1:10	0,04	—88
Na^+	10^{-2}	1:1000	0,36	+6	Cl^-	10^{-4}	1:10000	0,34	0
Mg^{2+}	10^{-3}	1:100	0,37	+9	NO_3^-	10^{-1}	1:100	0,39	+14
Ca^{2+}	10^{-3}	1:100	0,32	—6	ClO_4^-	10^{-3}	1:100	0,35	+3
Al^{3+}	10^{-3}	1:100	0,32	—6		—	—	0,34	Reference solution
Zn^{2+}	10^{-3}	1:100	0,33	—3					

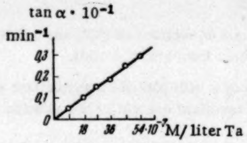

Fig. 1. Relation between reaction rate (1) and tantalum concentration. Concentrations of the solutions: KI—1.0 · 10^{-4} M; H_2O—1.0 · 10^{-3} M; H^+—0.16 M.

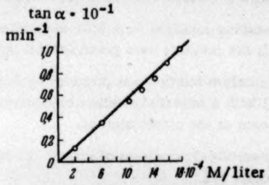

Fig. 2. Relation between reaction rate (1) and iodide concentration.

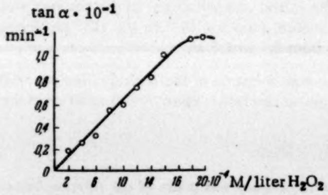

Fig. 3. Relation between reaction rate (1) and hydrogen peroxide concentration.

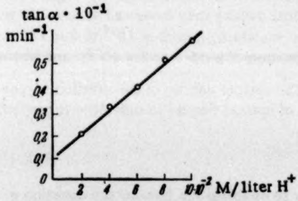

Fig. 4. Relation between reaction rate (1) and hydrogen ion concentration.

From this table it is clear that large amounts of cations and anions normally met, do not interfere with the determination of tantalum in solutions free from the ions of elements which catalyze the given reaction. Fluoride slows down the reaction by combining with tantalum to form a stable complex. The accelerating effect of nitrate is explained by traces of nitrite, which catalyzes the reaction.

Titanium and zirconium do not interfere with the reaction under the conditions indicated, since the oxalate complexes of these elements do not catalyze reaction (1). For the same reason, niobium, in equivalent amounts, or in amounts which are two-three times in excess, does not interfere with the determination of tantalum.

The rate of reaction (1) does not change essentially in the presence of sulfate ions, right up to a concentration of the latter of 0.1 M, accordingly, sulfate ions do not interfere with tantalum determination.

SUMMARY

A new and highly sensitive method has been developed for the quantitative determination of tantalum. The effect of certain ions on the accuracy of the method has been studied

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THE POLAROGRAPHIC PROPERTIES OF NIOBIUM IN PHOSPHORIC ACID SOLUTIONS

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The polarographic properties of niobium have been studied mainly in weak nitric acid solutions and in solutions of certain complexing agents. Thus, Zeltzer [1], and Portnov [2] obtained a wave for niobium in weak nitric acid solution. Stromberg and Reinus [3, 4] carried out a detailed study of nitric acid solutions of niobium, and found that the wave height is proportional to its concentrations in the range 0.2-4 millimoles/liter. Dhar [5] reduced niobium in nitric acid solutions in the presence of Cl^-, ClO_4^-, and SO_4^{2-}. Elson [6], Ferrett and Milner [7, 8] studied the behavior of niobium in solutions of oxalic, tartaric, citric, ethylenediaminetetraacetic acids and in other acids.

In recent years several papers have been published on the polarography of Nb^V in concentrated mineral acids. Cozzi and Vivarelli [9] found that niobium is reduced on the mercury cathode in hydrochloric acid solution.

Krylov, Kolevatova, and Samarina [10, 11] studied the polarographic properties of niobium in 70% sulfuric acid, and showed that niobium gives a well-defined wave on the dropping-mercury cathode, the height of the wave being proportional to the niobium concentration; cathodic reduction of Nb^V is irreversible under these conditions.

Gokhshtein [12] while studying the reduction of niobium in 70% sulfuric acid, showed that Nb^V gives a wave which is distorted by the discharge of hydrogen ions. In this connection,therefore, he recommends the use of an oscillographic polarograph, in which hydrogen ions do not have any effect, and the maxiumum current is proportional to niobium concentration.

The brief review shows that the polarographic properties of quinquevalent niobium on a dropping-mercury cathode in mineral acids have not been studied very much.

With the aim of extending the study of the polarographic properties of Nb^V in mineral acid solutions, we investigated solutions of niobium in orthophosphoric acid.*

Concentrated phosphoric acid (1.75) was used for this work since the author [13] had previously shown that niobium phosphates are soluble in solutions of concentrated mineral acids.

The niobium solutions were prepared from spectrographically pure niobium pentoxide, by fusing an aliquot of the latter with potassium bisulfate. After cooling, the melt was dissolved in 1% sulfuric acid. Niobium hydroxide was precipitated from this solution by means of ammonia, the precipitate was boiled, it was then cooled and filtered through a glass filter. The precipitate was washed with dilute ammonia until it was free from SO_4^{2-} ions. The niobic acid formed was dissolved in concentrated phosphoric acid and transferred to a standard flask in which the volume was made up to the mark with phosphoric acid and the whole thoroughly mixed. Polarographic measurements were carried out on a SGM-8 type polarograph made by the Geologorazvedka factory.

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*G. M. Veikes, a student at the Lenin Kazan State University, participated in the experimental work.

The galvanometer scale was calibrated by measuring the current passing through a KMS-6 resistance box connected into the circuit instead of the electrolytic cell; the voltage applied was 1000 volt. At a sensitivity of 1/10, 1 mm on the scale was found to correspond to 0.03 μA.

The electrolytic cell used was either an H-shaped vessel, into one arm of which was poured mercury to serve as the anode, or a 90 mm tall beaker, the bottom of which was covered with mercury. The surface area of the anode was greater than 5 cm^2 in both cases.

Curves were taken using a saturated calomel electrode ($S = 5\ cm^2$) as the external anode. The bridge consisted of a Π-shaped tube filled with concentrated phosphoric acid; the ends of the tube were closed with plugs of glass wool.

In order to eliminate the diffusion potential, connection was established through a vessel containing a saturated solution of potassium chloride.

Hydrogen was passed through the solutions for 15-20 minutes before taking the current-voltage curves. The hydrogen used was prepared by internal electrolysis [14].

The temperature of the solutions being polarographed was kept constant at 25° by means of an universal thermostat.

The relation between the limiting current and the half-wave potential, and the niobium concentration, are given in the Table and in Fig. 1. It is clear from the Table and from Fig. 1 that the limiting current (wave height) increases linearly with increasing niobium concentration of the solution.

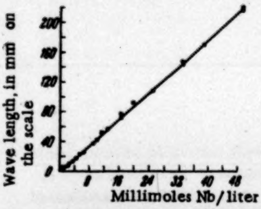

Fig. 1. Relation between the limiting current of niobium and the niobium concentration of the solution. Nb concentration expressed in millimoles/liter.

Relation between the Values of the Limiting Current and the Half-Wave Potential of Niobium in Phosphoric Acid Solutions, and the Niobium Concentration

$$(P = m^{2/3}\ \tau^{1/6} = 0.756\ mg^{2/3} \cdot sec.^{-1/2},\ \text{at } E = 1\ \text{volt})$$

Concentration of niobium in solution		Limiting current, in mm of the galvanometer scale (S = 1/5)	$\frac{I_d}{C_{Nb}}$, in mM/liter	$E_{1/2}$ (saturated calomel electrode)
g/liter	mM/liter			
0,046	0,5	4,4	8,8	0,610
0,0910	0,98	8,4	8,6	0,605
0,1132	1,2	8,8	7,4	0,605
0,221	2,38	17,2	7,3	0,600
0,354	3,54	25,8	7,3	0,615
0,4224	4,55	33,0	7,3	0,607
0,517	5,54	42,6	7,7	0,610
0,606	6,5	49,8	7,65	0,615
0,692	7,45	55,5	7,46	0,610
0,775	8,35	64,0	7,65	0,610
0,854	9,15	75	8,2	0,620
0,929	9,96	82	8,2	0,610
1,072	11,6	102	8,8	0,610
1,204	12,9	112	8,6	0,610
1,548	16,65	141	8,3	0,625
1,858	20	180	9,0	0,640
2,322	25	216	8,65	0,650
3,090	33,2	288	8,65	0,657
3,71	39,0	372	8,75	0,665
4,645	50	438	8,75	0,680
		Mean	8,1	0,622

The linear relation between the limiting current of niobium and its concentration in solution, together with the clearly defined wave (Fig. 2) permit niobium to be determined quantitatively in solution by a polarographic method.

The solutions are stable over a prolonged period (months) and give readily reproducible polarograms.

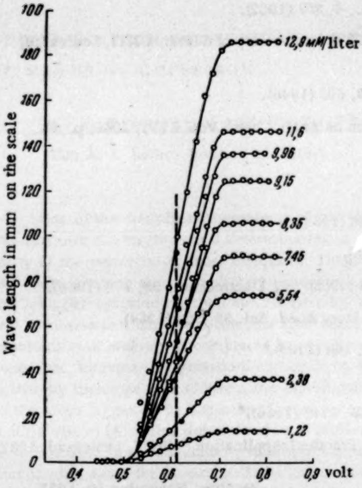

Fig. 2. Niobium waves in concentrated phosphoric acid for different niobium concentrations. Niobium concentration experssed in mM / liter.

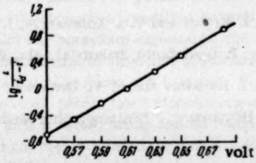

Fig. 3. Relation between the potential E and log $i/(i_d - i)$ for niobium (V) waves.

The general appearance of the i - E curves (Fig. 2) show that reduction of niobium proceeds in one stage. It is also clear from the Table that the half-wave potential ($E_{1/2}$) increases from 0.600 to 0.680 volt with respect to the saturated calomel electrode, with increasing niobium concentration.

In order to establish whether or not the electrode process is reversible, we calculated and constructed the curve relating log $i/(i_d-i)$ and the change in applied potential E (Fig. 3).

An examination of the results obtained (Fig. 3) shows that reduction of Nb^V from phosphoric acid solutions is irreversible. The slope has a value of 0.080, which differs essentially from the value calculated by means of the equation for a polarographic wave.

A study of the effect of diluting the phosphoric acid (1.75) with water showed that addition of 15% of water has no effect on the half-wave potential of niobium. Further addition of water leads to distortion of the niobium wave by the hydrogen wave. Addition of gelatine in amounts ranging from 0.01 to 0.1% showed no effect on the wave height.

Thus, phosphoric acid is preferable to nitric and sulfuric acids as a supporting electrolyte for the polarographic determination of niobium. Solutions of niobium in phosphoric acid are stable, and give a clearly defined wave for niobium within the concentration range 0.2-50 millimoles / liter. When nitric acid is used, the linear relation between the limiting current and niobium concentration only holds for the concentration range 0.2 to 4 millimoles/ liter, while in sulfuric acid solutions the niobium wave is distorted by the discharge of hydrogen ions. Studies of the polarographic properties of niobium and of the elements which accompany it, in acid solutions, continue.

SUMMARY

A polargraphic study of phosphoric acid solutions of niobium has been carried out for the first time. It has been established that in concentrated phosphoric acid (1.75), niobium gives a clearly defined wave. The value of the limiting current is linearly related to the niobium concentration over the concentration range 0.5 to 50 millimole/ liter. Solutions of niobium in phosphoric acid are stable and give readily reproducible polarograms.

The half-wave potential $E_{1/2}$ increases from 0.600 to 0.680 volt (with respect to the saturated calomel electrode) as the niobium concentration increases (from 0.5 to 50 millimole/liter).

Reduction of Nb^{V} in phosphoric acid solutions is irreversible.

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**Russian translation.

DETERMINATION OF NIOBIUM IN THE PRESENCE OF TUNGSTEN BY MEANS OF CUPFERRON

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One of the complicated problems of analytical chemistry is the separation of niobium and tungsten. The difficult of carrying out a determination of niobium in the presence of tungsten is explained by the similarity of the properties of these elements. Tungsten, like niobium, gives oxides which are insoluble in water, and while carrying out the hydrolytic separation of niobium, tungsten also separates out [1]. Schoeller, Powell, and Jahn [2] separated niobium and tungsten by means of a mixture of magnesium sulfate, ammonium chloride, and ammonia in a carbonate solution after fusing tungsten and niobium oxides with potassium carbonate. Determination of niobium is completed by precipitation with tannin. Golubtsova [3] modified Schoeller's method somewhat, by replacing potassium carbonate by a mixture of sodium and potassium carbonates; the fusion rate is thereby increased. In addition, she established that increasing the amount of ammonia added to 5 ml, instead of the drops suggested by Schoeller, favors a more complete separation of niobium and tungsten. Budanova and Gavrilova [4], during determination of niobium and tungsten in steel, precipitated niobium together with iron, tantalum, and vanadium by means of cupferron in a sulfuric acid medium, using sodium fluoride as a complexing agent for tungsten. Under these conditions niobium is not precipitated completely quantitatively. Determination of niobium is completed by the acid hydrolysis method.

Our problem was to develop a method for determining niobium in alloys, steels, and other products containing tungsten, without having to resort to a preliminary separation of niobium and tungsten.

In order to study the conditions for precipitating and separating niobium from tungsten by means of cupferron, we prepared three standard solutions of niobium with oxalic acid, ammonium oxalate, and tartaric acid, respectively. The standard tungsten solution was prepared from sodium tungsten.

To accurately measured volumes of the standard niobium solution containing from 0.8 to 4.5 mg Nb, was added various amounts of the standard tungsten solution containing from 30 to 125 mg of W. The ratios of Nb : W were 1 : 25 and 1 : 35. The solutions were diluted with water to 100-150 ml, acidified with 5 drops of hydrochloric acid (sp. gr. 1.19) and the niobium precipitated with 10-20 ml of a 3% aqueous solution of cupferron; the latter was added slowly, dropwise, the solution being stirred continuously. A small amount of macerated paper was then added and the solution stirred until the precipitate had been completely coagulated. The precipitate was filtered through a 7-9 cm diameter paper (white band) and washed 5-6 times with cold water containing 20 ml of 3% aqueous solution of cupferron and 1 ml of hydrochloric acid (sp. gr. 1.19) per liter; the precipitate was then ashed in a platinum crucible or basin, and heated in a muffle until all the carbon of the filter paper had been burnt off; the residue was fused with 1-2 g of potassium pyrosulfate over a small burner flame to avoid sputtering. On cooling, 10-20 ml of a 4% oxalic acid or ammonium oxalate solution, or 10% tartaric acid was added to the contents of the crucible or basin and the contents of the crucible or basin heated on a sand bath until the melt had dissolved. This solution was transferred to a 250-300 ml beaker and the volume adjusted to 100-150 ml, this liquid was acidified with 5 drops of hydrochloric acid and the niobium precipitated as described above. Filter and precipitate were placed in a tared platinum or porcelain crucible in which they were ashed, the ash was then heated for 5-10 minutes at 1000° and niobium weighed as the pentoxide.

Niobium was precipitated with cupferron at room temperature. The precipitate was filtered rapidly, washed thoroughly, and was readily transferred onto the filter.

Results for the determination of niobium in a standard solution, in the presence of tungsten, are given in Table 1.

TABLE 1

Determination of Niobium in the Presence of Tungsten in a Standard Solution

Complexing agent	Amount taken, in mg		Nb, found, in mg	Difference, in mg
	W	Nb		
Tartaric acid	30	0,84	0.84	0,00
	30	0.84	0.98	+0,14
	60	0,84	0,91	+0,07
	50	1,68	1.75	+0,07
	50	1,68	1.68	0,00
	50	1.68	1,75	+0,07
	100	4,48	4,55	+0,07
	100	4,48	4,55	+0,07
Ammonium oxalate	30	2,17	2,24	+0,07
	30	2,17	2,17	0,00
	30	2,17	2,10	—0,07
	60	2,17	2,24	+0,07
	60	2,17	2,24	+0,07
	60	2,17	2,31	+0,14
	50	4.48	4,27	—0,21
	50	4,48	4,55	+0,07
	50	4,48	5,55	+0,07
	100	4,48	4,55	+0,07
	100	4,48	4,55	+0,07
Oxalic acid	100	4,48	4,62	+0,14
	100	4,48	4,55	+0,07
	100	4,48	4,48	0,00
	125	4,48	4,48	0,00
	125	4,48	4,27	—0,21

These results show that any of the complexing agents listed above can be used for determination of niobium in the presence of tungsten. On the basis of the results obtained, the following experimental procedure is suggested.

Determination of niobium in the ternary alloy W–Si–Nb. 0.1 g of test material is placed in a platinum basin, and 2-3 ml of hydrofluoric acid is added; this is followed by nitric acid which is added slowly in order to avoid too vigorous a reaction; nitric acid is added until the alloy has dissolved completely. The contents of the basin are evaporated to dryness on a sand bath, and the dry residue fused with 2-3 g of potassium pyrosulfate. 30-40 ml of a 4% solution of oxalic acid, or ammonium oxalate or tartaric acid is added to the contents of the basin, and the mixture is heated on a sand bath and 30-40 ml of water then added; heating is continued until the melt has dissolved. The solution is transferred to a 250-300 ml beaker and the basin rinsed with cold water, the volume being made up in this way to 150-200 ml; 5 drops of hydrochloric acid (sp. gr. 1.19 is added, and the niobium is precipitated with 20-25 ml of a 3% aqueous solution of cupferron. Cupferron is added slowly with continuous stirring of the solution. A small amount of macerated paper is added and the solution carefully stirred until the precipitate has coagulated completely. The precipitate is filtered through a 7-9 cm diameter filter paper (white band) and washed 6-8 times with cold water containing 20 ml of the 3% aqueous solution of cupferron and 1 ml of concentrated hydrochloric acid per liter; the precipitate is thereby transferred quantitatively onto the filter paper. Filter paper plus precipitate are then returned to the basin in which it is ashed, and then calcined in a muffle at 500-600° until the carbon on the paper has been burnt off completely. The residue is fused with 1-2 g of potassium pyrosulfate, according to the amount of the residue, fusion being carried out over a small flame; 20-30 ml of 4% oxalic acid is added to the contents of the basin and the whole heated, 20-30 ml of water is then added and heating continued until the melt has dissolved; the contents of the basin are transferred to a beaker, 5 drops of hydrochloric acid is added and reprecipitation carried out as described above. Filter paper and precipitate are placed in a tared platinum or porcelain crucible in which they are then ashed; the ash is calcined for 15-20 minutes at 1000°, and then allowed to cool in a desiccator and finally weighed as niobium pentoxide. The conversion factor from Nb_2O_5 to Nb is 0.6990.

Results for the determination of niobium in this alloy are given in Table 2.

TABLE 2

Reproducibility of the Results for the Determination of Nb in Alloys Containing from 36 to 70% of W

Sample	Nb, in %		
32	50,64	50,70	50,76
33	42,50	42,51	42,75
34	34,16	34,17	34,73
35	21,38	21,47	21,50
36	12,42	12,96	13,05

Tungsten can be determined in the filtrate after removal of the niobium. For this purpose, both the filtrates are combined and the oxalic acid destroyed, and, where necessary, the cupferron also; tungsten is then determined by one of the known methods.

In order to check on the completeness of the separation of niobium from tungsten, we examined the separated precipitate of niobium pentoxide for its tungsten content, using the radioactive indicator W^{185} for this purpose.

To a dissolved aliquot (0.1 g) of the ternary alloy W–Si–Nb was added an active solution containing the radioactive isotope of tungsten W^{185} with a known specific activity. All the operations enumerated in the technique described above were then repeated. The calcined and weighed residue of niobium pentoxide was fused with 1-2 g of potassium pyrosulfate, and the melt obtained dissolved in 15 ml of 4% oxalic acid in a 25 ml standard flask; the volume of this solution was made up to the mark with water. 0.2 ml of this solution was placed on an aluminum plate, and, after drying, the activity was measured on a B torsion counter. From this activity it was then possible to assess the amount of tungsten which had been coprecipitated with the niobium pentoxide. Results of these experiments are given in Table 3.

TABLE 3

Examination of the Isolated Residues of Niobium Pentoxide for their Content of Tungsten by means of the Radioactive Tungsten Isotope W^{185}

Test material	Amount taken, in mg		Activity of the original solution, in impulses/minute	Niobium pentoxide residue activity after tungsten separation	Amount of W found in the niobium residue, in mg
	Nb	W			
Standard solution	4,48	60	1 095 200	Background	0,0
	4,48	100	1 095 200	Background	0,0
	8,96	160	1 095 200	2375	0,2
	8,96	00	1 095 200	Background	0,0
Alloy	12,96	70	1 105 400	1375	0,1
	13,05	70	1 249 200	3000	0,2
	42,75	40	1 105 400	8875	0,8
	34,16	55	1 157 100	20 250	1,7

By means of this experiment it was established that the amount of tungsten trapped by the niobium precipitate depends on the amount of the latter. During precipitation of 5 and 10 mg of niobium in the presence of 100 mg of tungsten, the niobium pentoxide obtained was found to be pure, and did not contain any tungsten.

During the examination of the niobium pentoxide residues obtained from the alloys, it was observed that coprecipitation of tungsten commences at niobium contents in excess of 30%.

Determination of niobium in steels containing tungsten. During the determination of niobium in steels and other materials containing, in addition to tungsten, other elements such as iron, titanium, vanadium and elements which are also precipitated by cupferron, it is recommended that niobium be precipitated beforehand with tannin in the presence of ascorbic acid, according to a method which we have developed previously [5].

1-2 g of steel is dissolved by boiling the sample with 20-25 ml of hydrochloric acid (1 : 1) in a 300 ml beaker. 5 ml of nitric acid (sp. gr. 1.40) is then added in order to oxidize the elements, boiling is continued and the solution evaporated almost to dryness. 30 ml of hydrochloric acid (1 : 2) is added and the whole boiled until complete removal of nitrogen oxides. If, during the boiling operation, the volume of the solution should decrease by 1/3, then 10-20 ml of water is added so as to preserve the requisite hydrochloric acid concentration. The solution is diluted with water to 180-190 ml, and, without paying attention to the occasional presence of a light-black precipitate, 1-2 g of ammonium chloride is added, followed by 0.1-0.2 g of ascorbic acid, and the whole is heated to the boil. To the hot solution is added (dropwise) 10 ml of a freshly prepared 1% aqueous solution of tannin (tannin dissolves in hot water) with continuous stirring. Tungsten is thereby coprecipitated. The solution is kept at the boiling point for 2-3 hours until the precipitate has coagulated completely; a small amount of macerated paper is added, and, after the solution has cooled (it can be left overnight) the precipitate is filtered through a 7-9 cm filter paper (white band), and then washed 6-8 times with a cold 4% solution of hydrochloric acid. Filter paper plus precipitate are placed in a platinum crucible and ashed, crucible and contents are then heated in a muffle at 500-600° until all the organic materials have been burnt off. The residue is moistened with water and 2-3 ml of sulfuric acid (1 : 1) and 2-3 ml of hydrofluoric acid added; the crucible is placed on a sand bath and heated, gently at first, until the precipitate has dissolved, it is then heated more strongly until white fumes of sulfur dioxide appear. After the sulfur dioxide fumes have been coming off for 10 minutes, the crucible is cooled and 1-2 ml of water added, and the evaporation is repeated until no more than 2-3 drops of sulfuric acid remain in the crucible (evaporation to dryness must be avoided). Silica is removed in this way, and any particles remaining undissolved after treating the steel with hydrochloric and nitric acids are broken down completely. On cooling, 10 ml of hydrochloric acid (1 : 1) is added to the contents of the crucible and the whole heated until the salts dissolve. The solution is transferred to a 100 ml beaker and the crucible rinsed out several times with cold water, 0.05-0.1 g of ascorbic acid is added and the solution diluted with water to 80-90 ml; the solution is then heated to the boil and the niobium reprecipitated with tannin as described above.

The precipitate is ignited in a platinum basin and fused with 1-2 g of potassium pyrosulfate; 10-20 ml of 4% oxalic acid is added to the contents of the basin and the mixture heated until the melt has dissolved, niobium is then determined by the method described above for the determination of niobium in tungsten alloys.

SUMMARY

A rapid and accurate method is suggested for the determination of niobium in the presence of large amounts of tungsten. In contrast to existing methods, this method is highly accurate and does not require the preliminary separation of niobium and tungsten. The method is based on the precipitation of niobium with cupferron in a weakly hydrochloric acid medium in the presence of oxalic acid which forms a complex compound with tungsten.

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A NEW LUMINESCENT METHOD OF MICROCHEMICAL ANALYSIS (CRYSTALLOPHOSPHOR). COMMUNICATION 1. DETECTION OF ANTIMONY

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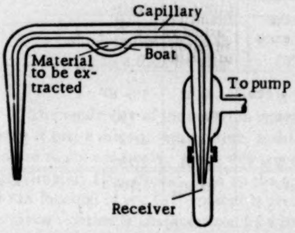
The exceptionally high sensitivity of luminescent reactions which makes it possible to work with micro- and ultramicro amounts of material ($10^{-12} - 10^{-15}$ g) permits their use in microchemistry. Only microcrystalloscopic, and to some extent spot (catalytic), reactions can compete with luminescent reactions.

The basic aim of our work was to develop new luminescent reactions based on the preparation of crystallophosphors, and to develop microchemical methods using these crystallophosphors.

Spot and microcrystalloscopic luminescent analysis do not differ from the usual microchemical analysis from the point of view of the techniques used for carrying them out. The ultraviolet source used was a PRK-4 mercury-quartz lamp. A capillary with an internal diameter of 0.1 mm for its drawn-out tip was used for sampling a few thousandths of a ml. For working with larger volumes, a micro test tube with a capacity of 0.1-0.2 ml was used. Removal of precipitates was carried out by filtration and centrifuging. The first technique was used during work on object glasses, the second technique being more suitable for work with capillaries and micro test tubes. We constructed a centrifuge capable of 6000 revolutions/minute for removing precipitates by centrifuging. The centrifuge consisted of a small motor, and an ebonite disc with horizontal sockets, and a guard ring. When such a centrifuge was used, 5-10 seconds was sufficient for removing crystalline precipitates.



Detection of antimonyon calcined calcium oxide. The reaction is based on the formation of a crystallophosphor $CaO \cdot Sb$, which on being irradiated with ultraviolet light shines with a yellow-green color.

In order to prepare the calcium oxide, chemically pure calcium carbonate is calcined in a muffle and then triturated with water until a thick paste is obtained. The paste contained in a basin is placed in a desiccator on the floor of which water is poured. Using a platinum or nichrome loop, a drop of this paste is taken and calcined in a burner flame. The calcium oxide thus prepared is cooled and checked for purity by subjecting it to the action of ultraviolet radiation. The "pearl" formed should be colored a universal red. If there should be any luminescence this indicated that the original calcium carbonate is not pure enough. Such calcium carbonate should not be used, otherwise incorrect results will be obtained. When a sufficiently pure bead has been obtained, a drop of test solution containing the smallest possible amount of acid to keep the antimony in solution, is placed on it. The calcium oxide bead is then calcined again in such a way that the place on which the test solution has been placed is turned towards the side of the flame, and the bead examined again in the ultraviolet light. When antimony is present a luminescence is observed, the color of which changes with the antimony concentration; when fairly large amounts of antimony are present the color is greenish-yellow, while when small amounts are present the color is a whitish-yellow (Table 1).

The sensitivity of this reaction, as shown in Table 1, is characterized by a limit of identification equal to 0.000001 γ of antimony at a limiting dilution of $1:10^{10}$.

Bismuth, lead, uni- and divalent mercury, thallium, molybdenum, selenium, tellurium, and tungsten also form crystallophosphors with calcium oxide. Their basic characteristics are given in Table 2. Detection of antimony in the presence of these elements is only possible when the absolute content of these materials in the drop of test solution does not exceed a certain maximum amount. These numerical amounts are given in Table 3.

TABLE 1

Color and Intensity of the Illumination of CaO · Sb Phosphors as a Function of the Antimony Content

Sb content (γ) of a 0.01 ml drop	Color of the luminescence	Intensity of the illumination
81.5	Greenish-yellow	Bright
8.15	Greenish-yellow	Bright
0.815	Greenish-yellow	Bright
0.081	Gradual transition	Gradual decrease in intensity
0.008		
0.001		
0.0001		
0.00001		
0.000001	Pale-yellow	Weak

TABLE 2

Formation of Crystallophosphors Based on CaO

Activator	Color of the luminescence	Limit of identification (γ) in a drop of 0.01 ml	Limiting dilution	Activator	Color of the luminescence	Limit of identification (γ) in a drop of 0.01 ml	Limiting dilution
Bi^{3+}	Blue-violet	0,02	$1;10^6$	Tl^+	Yellow-green	0,02	$1:5\cdot10^5$
Pb^{2+}	From bluish-white to lilac	0,01	$1:10^6$	Mo^{VI}	Turquoise	67,0	1:150
Hg_2^{2+}	From yellow to blue-white	0,02	$1:5\cdot10^5$	Se^{2-}	Red	0,04	$1:10^6$
Hg^{2+}	From yellow to blue-white	0,002	$1:5\cdot10^6$	Te^{2-}	Red	0,04	$2:10^6$
				W^{VI}	Rose-red	100,0	1:100

Manganese, cobalt, nickel, copper, trivalent chromium, and iron do not form crystallophosphors with CaO, but strongly interfere with the detection of antimony by extinguishing, or strongly weakening, the luminescence which develops. The limiting ratios for these elements during the detection of trivalent antimony in a 0.01 ml drop are as follows:

Sb : Mn = 1 : 300000 at 10^{-4} and 10^{-5} γ Sb
Sb : Co = 1 : 300000 at 10^{-4} γ Sb
Sb : Ni = 1 : 3000000 at 10^{-4} and 10^{-5} γ Sb
Sb : Cu = 1 : 200 at 0.815 γ Sb
Sb : Cu = 1 : 1500 at 0.01 γ Sb
Sb : Cu = 1 : 150000 at 10^{-5} γ Sb
Sb : Cr = 1 ; 30 at 0.815 γ Sb

Sb : Cr = 1 : 300 at 0.008 γ Sb.
Sb : Cr = 1 : 2600 at 10^{-3} and 10^{-4} γ Sb
Sb : Fe = 1 : 75 at 0.815 γ Sb
Sb : Fe = 1 : 800 at 0.008 γ Sb
Sb : Fe = 1:60000 at 10^{-4} and 10^{-5} γ Sb

Detection of antimony by means of potassium ferrocyanide. Detection of antimony by means of $K_4Fe(CN)_6$ is carried out by a microscrystalloscopic reaction in filtered ultraviolet light. The order in which the individual operations are carried out has a considerable effect on the sensitivity of this reaction.

A drop of reagent solution and a drop of test solution are placed on an object glass; the drops are mixed. By drying the liquid slowly, well-formed crystals which strongly absorb ultraviolet radiation separate out. As long as the deposit remains damp, no illumination is observed. As the deposit dries out, a beautiful luminescence with a yellow color and which is very intense at high concentrations, develops. Excitation of the light occurs under the influence of ultraviolet radiation with $\lambda > 313$ mμ. It is the crystal edges which luminesce most.

The reaction can be speeded up as follows: drops of reagent and test solution are placed on a quartz object glass and the mixture dried rapidly. The reaction can be carried out quite well with amounts of antimony not less than 1.0 γ in a drop of 0.01 ml.

TABLE 3

Detection of Antimony in the Presence of Elements which Form Similar Crystallophosphors with CaO

Element	Pb^{2+}	Hg^{2+}	Hg^{2+}	Te, Se	Mo^{VI}	W^{VI}
Absolute content (γ) in a 0.01 ml drop	Less than 0.00104	Less than 0.00002	Less than 0.00002	Less than 0.0025	Less than 60.0	Less than 100.0
Absolute content of Sb (γ) in a 0.01 ml drop	10^{-5}	10^{-5}	10^{-5}	10^{-5}	10^{-5}	10^{-5}

The sensitivity of the reaction can be increased by placing a drop of the reagent on an object glass and drying it out; a drop of test solution is then placed on the still hot dry spot formed by the reagent and this allowed to dry out freely. When this sequence of operations is followed, the sensitivity can be increased by approximately 1000 times. Data on the color and illumination intensity of the crystallophosphor $K_4[Fe(CN)_6] \cdot Sb$ as a function of the Sb^{3+} content is given in Table 4. It follows from these results that the sensitivity of the given reaction is characterized by a limit of identification of 0.001 γ of antimony ions at a limiting dilution of $1:10^7$.

Only arsenic ions give a similar reaction (limit of identification for arsenic ions, 0.12 γ at a limiting dilution of $1:8.3 \times 10^4$). Since many elements form precipitates with $K_4[Fe(CN)_6]$, it is necessary to separate most of the elements in order to carry out the above reaction successfully. Such a separation can be effected by extraction antimony from hydrochloric acid solutions with diethyl ether.

The limiting ratios of antimony to tin, germanium, and copper at which it is still possible to detect trivalent antimony without separating it from these elements are as follows:

Sb : Sn = 1 : 280 at 0.08 γ Sb
Sb : Sn = 1 : 2800 at 10^{-3} γ Sb
Sb : Ge = 1 : 120 at 0.008 γ Sb
Sb : Cu = 1 : 1 at 8.15 γ Sb

Decomposition of antimony ores and alloys and separation of antimony from accompanying elements. Breakdown of ores by fusion with sodium carbonate and sulfur. 3-5 mg of test material is placed in a No. 1 porcelain crucible and five times its amount of a 1 : 1 mixture of sodium carbonate and sulfur added, and the whole mixed thoroughly. A fine layer of the soda-sulfur mixture is strewn on top and the crucible covered with a lid; it is then uniformly heated from below, after 2-3 minutes the flame temperature is increased, and finally the crucible is heated until all the sulfur has been burnt off. After the melt has cooled it is leached with water. 0.1-0.2 ml of the solution plus precipitate is taken and centrifuged. Centrifugate and wash liquors are transferred to a micro test tube; acetic acid is added, followed by 1-2 drops of a saturated solution of tin chloride (for removing arsenic) and 4-5 drops of concentrated hydrochloric acid. The mixture is heated on a water bath. The insoluble residue is centrifuged, and the antimony extracted from solution by extraction (see below).

TABLE 4

Color and Intensity of the Illumination of $K_4Fe(CN)_6 \cdot Sb$ Phosphors as a Function of the Antimony Content

Antimony content (γ) in a 0.01 ml drop	Color of the luminescence	Intensity
81.5	Bright yellow	Strong
8.15	Bright yellow	Strong
0.815	Gradual appearance of a yellow-green and bluish luminescence	Decreasing intensity of illumination
0.081		
0.008		
0.001	Yellow, blue in spots	Quite distinct

Decomposition of oxide rocks. 3-5 mg of sample is placed in a micro crucible and 8-10 drops of a saturated solution of Rochelle salt added. The precipitate is brought into suspension and then heated. Boiling is stopped 7 minutes after the mixture has come to the boil. 0.1-0.2 ml of the solution with the precipitate suspended in it is taken and centrifuged. The precipitate is washed with 3-5 drops of water containing Rochelle salt, and the mixture centrifuged again; this centrifugate is then combined with the previous one. The solution obtained is acidified with hydrochloric acid, and the walls of the micro test tube rubbed gently with a glass rod. After some time a copious precipitate of potassium bitartrate is formed; antimony is precipitated with this as the oxychloride. The precipitate is filtered off and dissolved in the smallest possible amount of 6N HCl, and the antimony extracted. If the solution contains arsenic or trivalent iron, then $SnCl_2$ and fuming hydrochloric acid are added to the solution, the whole is heated, and the precipitate centrifuged.

Decomposition of alloys. 3-5 mg of sample is placed in a micro crucible and mixed with 5-10 times its amount of a mixture of NH_4Cl and NH_4NO_3 (2 : 1); the whole is then heated until the sample has almost broken down completely. The melt obtained is dissolved in water strongly acidified with hydrochloric acid, and the solution centrifuged. A small aliquot of the centrifugate is taken and its iron content determined; if the iron content is low then 2-3 drops of 0.5 M ferric chloride solution is added. The solution is heated and excess ammonia added; the ferric hydroxide precipitate formed traps all the antimony from the solution. This precipitate is separated by centrifugation and dissolved in 1-2 drops of a solution of $SnCl_2$ in concentrated HCl. The antimony is extracted from the centrifugate by means of diethyl ether.

Extraction. Only 66% of the antimony passes into the ether layer when extraction is carried out once. Seven extractions are necessary to extract 99.95% of the antimony. When only a small amount of liquid is to be extracted it is best to carry out extraction in a continuous flow of liquid. For this purpose we used the extractor shown in the diagram. The material to be extracted is placed in the boat of the extractor in such an amount that its wetting edges are slightly lower than the opening of the capillaries. Suction is applied by means of a syringe with a screw-feed piston. Extraction is carried out by dipping the drawn-out tip of the extractor in a vessel of ether, and the ether gradually sucked up. Subsequently, when the boat has been loaded, the ether is sucked through in small portions. As the ether accumulates in the receiver, the ether is distilled off by placing the receiver in a beaker with hot water and air sucked through. Using this technique evaporation proceeds without bumping. For greatest efficiency of extraction the solution should be 6N with respect to HCl.

These luminescent reactions which have been suggested for the detection of antimony have been tried out on pure salts, sulfide rocks, dolomite rocks, on bronze-type alloys, and also on pure antimony metal. The antimony content varied from 0.001 to 3.0% (with the exception of antimony metal). All tests gave uniformly positive results.

SUMMARY

A technique is described for carrying out luminescent microchemical analysis, which is based on the formation of crystallophosphors.

New luminescent reactions for the microchemical detection of antimony are described which are based on the formation of the crystallophosphors $CaO \cdot Sb$ and $K_4[Fe(CN)_6] \cdot Sb$.

The possibility has been demonstrated of using the reactions described above for the qualitative analysis of mineral raw materials and alloys.

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DETERMINATION OF SMALL AMOUNTS OF LEAD IN ROCKS

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The analytical determination of small amounts of lead consists of the following three successive operations: 1) decomposition of the sample, 2) concentration of the lead, and 3) its final determination in a small volume of solution prepared by some technique or other. In choosing a method for breaking down the sample, it is important to bear in mind that lead may be present in the crystalline lattice of silicates, so that the decomposition of the sample should be as complete as possible. It is usually recommended that the sample be broken down with hydrofluoric acid mixed with sulfuric, perchloric, or nitric acid. Fusion of the sample with various fusion mixtures, or distillation of the lead by heating with a reducing agent, are techniques which are less often used.

Concentration of lead can be effected by variants of the method of extraction by coprecipitation with various collectors, or by extraction of certain inner-complex compounds of lead by organic solvents, or by electrolysis methods; sometimes a combination of these methods is expedient. Thus, lead has been coprecipitated with silver sulfide [1], strontium sulfate [2], barium sulfate [3], barium chromate [4], and with the fluorides of the rare earths and calcium [5]. In the extraction methods, use is made of the solubility of the compound of lead with diphenylthiocarbazone (dithizone) in chloroform or carbon tetrachloride [6]. This method has been recommended by several authors for the extraction of lead during the analysis of rocks [7, 8]. The compound of lead with sodium diethyldithiocarbamate has been suggested for separating lead from foodstuffs [9, 10].

Of other methods for separating lead, mention should be made of the distillation of lead by heating in a current of hydrogen [11], and in a vacuum in the presence of carbon [5, 16].

Whatever methods are used for breaking down the sample and for concentrating the lead, particular attention must be given to the possibility of loss of some of the lead by adsorption on the vessel walls and filter paper, and, on the other hand, to the possibility of the introduction of traces of lead with the reagents, most of which contain very small amounts of lead, and require careful purification [2, 7]. Reagents should be stored in quartz flasks or in flasks made from polyethylene or fluoro plastics. In all cases, blanks must be carried out so as to apply the necessary corrections to the experimental results.

Lead can be finally determined with satisfactory accuracy either photometrically or polarographically. Of the photometric methods, mention can be made of the sulfide [13], tetramethyldiphenylmethane [7], rubeanate [14], and dithizone methods. The dithizone method is the most sensitive; in addition, this method combines the extraction of lead dithizonate with its determination [7].

Polarographic determination of lead in a concentrate permits small contents of lead to be determined with high accuracy. Metals whose half-wave potentials coincide, or are similar to that of the lead, interfere with the polarographic determination of lead. Removal of interfering elements is partially achieved during the concentration stage, and can also be partially achieved by complexing these elements [12].

We have investigated the following methods of concentrating lead from the point of view of their application to the analysis of rocks:

1) Extraction of lead dithizonate with chloroform or carbon tetrachloride from an ammoniacal citrate solution, obtained directly after decomposition of a sample with hydrofluoric acid mixed with nitric or perchloric acid.

2) Extraction of lead from solution, based on its coprecipitation with mercuric sulfide or zinc sulfide.

3) Extraction of lead from solution, based on its coprecipitation with barium sulfate, with subsequent final separation of lead by extraction of lead dithizonate with an organic solvent.

4) Extraction of lead diethyldithiocarbamate with a mixture of pentanol and toluene.

5) Heating a mixture of the sample mixed with carbon in a vacuum, or in a stream of nitrogen in order to distill off the lead.

The percentage extraction of the lead was followed in most instances radiochemically.

Lead was finally determined polarographically, and by photometric determinations of solutions of the dithizonate extract.

For the polarographic determination of lead in rocks at the level of some thousandths of a percent, 1-2 g of sample was taken. The volume of the solution polarographed was 3-5 ml. The supporting electrolyte in most cases was a 0.1 N solution of potassium nitrate and nitric acid. The cathode was a dropping mercury electrode, while the anode was a saturated calomel electrode. Electrolytically prepared hydrogen was passed through the solution prior to polarograms being taken.

Colorimetric determination of lead was carried out on 0.1-0.2 g of sample

1. Separation of lead by extraction of lead dithizonate. An aliquot of the rock was broken down with a mixture of hydrofluoric and perchloric or nitric acids. A radioactive indicator (RaD) was added to the solution. After removal of the acids, the residue was dissolved on heating in dilute hydrochloric acid. To this solution was added 25 ml (30-40%) of an aqueous solution of ammonium citrate. The pH was adjusted to 8.5-10 by addition of ammonia. Lead was extracted with this solution by shaking the latter with several portions of a 0.01-0.02% solution of dithizone in chloroform, until the layer of the latter had a green color. The solution of the dithizonates was washed free of traces of ammonia solution by means of twice-distilled water. Lead was re-extracted from the organic solvent by shaking the latter with dilute nitric acid (0.02 N). The nitric solution was freed from traces of dithizone by shaking it with chloroform. The chloroform was discarded and the nitric acid solution evaporated to dryness. The activity of the residue obtained was then determined; the residue was dissolved in the supporting electrolyte and the lead content of the concentrate determined polarographically.

As experiment showed, the percentage extraction of lead by the method outlined above was, on an average, 91%.

Quantitative determination of lead isolated by the method indicated above from aliquots of 0.1-0.2 g was carried out photometrically.

2. Separation of lead by coprecipitation with sulfides. a) Coprecipitation with mercuric sulfide. Mercuric sulfide is a suitable collector because it is easy to remove the mercury from the concentrate obtained, by heating the latter. Mercuric nitrate (sufficient to give about 0.1 g of mercury) was added to the solution prepared in the appropriate way. Mercuric sulfide was then precipitated from the hydrochloric acid solution (0.4 N) by hydrogen sulfide. The solution plus precipitate was allowed to stand overnight, it was then filtered off, washed with hydrogen sulfide water, and ashed; the precipitate was heated to remove the mercury. The residue in the crucible was dissolved in dilute nitric acid.

Lead was finally separated by extracting it with a chloroform solution of dithizone from an ammoniacal citrate solution. The lead content of the concentrate was determined polarographically.

Experiments showed that 60-70% of the lead present is extracted when this technique is used.

b) Coprecipitation with zinc sulfide. Zinc (in the form of a zinc chloride solution) corresponding to 25-30 mg (on a metal basis) was added to the solution prepared in the appropriate way; the solution was then made weakly acid with respect to acetic acid (about 1%) and the zinc precipitated as sulfide with hydrogen sulfide; the lead was thereby coprecipitated with it. 1 ml of a 1% gelatine solution was added to improve coagulation of the precipitate. After standing overnight the precipitate was filtered off, washed with hydrogen sulfide water, and dissolved in hot 2 N hydrochloric acid. Lead was finally determined polarographically; the supporting electrolyte used was hydrochloric acid, or a solution of potassium chloride in hydrochloric acid.

Experiments showed that about 80-90% of the lead can be coprecipitated with zinc sulfide under the conditions we used.

3. Separation of lead by coprecipitation with barium sulfate. Coprecipitation of lead was carried out under the conditions recommended by Starik [3].

Alcohol was added to depress the solubility of the lead sulfate. Starik carried out a final separation of lead from the precipitated sulfates by an electrolytic method. Our experiments showed that very small amounts of lead are more conveniently separated by extraction of lead dithizonate with chloroform.

A sample of rock was broken down with hydrofluoric acid. After decomposition of the sample, a standard solution of RaD was added to it; this was followed by 1-2 ml of 0.1 N barium chloride and concentrated sulfuric acid. The mixture was heated to remove traces of hydrogen fluoride. The residue was dissolved in boiling water acidified with hydrochloric acid. The solution was diluted with an equal volume of ethanol and allowed to stand overnight. The precipitated sulfates were filtered off and washed, and, after ashing, fused with sodium carbonate. The melt was leached with water, and the precipitated carbonates filtered off and carefully washed. The washed precipitate was dissolved in dilute nitric acid. To the acid solution was added 5-10 ml of a 25% solution of ammonium citrate, formed by ammonia until the blue color of thymol blue indicator appeared; a 0.02% solution of dithizone in chloroform was finally added.

To the alkaline filtrate was added 3-5 ml of ammonium citrate followed by nitric or hydrochloric acid until the greenish color of the thymol blue indicator appeared. A 0.002% solution of dithizone in chloroform was used for extracting the lead.

The extracts of lead dithizonate from both solutions were combined and the lead then determined as indicated above.

Tests showed that an average of 76% of the lead can be extracted by this technique.

4. Extraction of lead by extraction as lead diethyldithiocarbamate. Sodium diethyldithiocarbamate has been recommended for the separation of lead during the analysis of foodstuffs [9].

We adopted this method for analyzing rocks, using the technique described for organic materials [10]. According to this method, a reagent containing sodium citrate, sodium bicarbonate, and sodium diethyldithiocarbamate is added to a weak hydrochloric acid test solution. Subsequently the lead diethyldithiocarbamate (together with the diethyldithiocarbamates of the other metals) is extracted with a mixture of equal volumes of pentanol and toluene at a pH of 7. The pentanol-toluene mixture readily dissolves the diethyldithiocarbamates of all the reacting metals, and allows one to avoid the formation of a precipitate of the diethyldithiocarbamates of other metals, in particular of iron, which are sparingly soluble in pentanol alone. Lead is re-extracted from the organic solvent by means of dilute hydrochloric acid. The hydrochloric acid solution of lead is poured into an aqueous ammoniacal solution of dithizone containing potassium cyanide and sodium metabisulfite. On shaking this solution with carbon tetrachloride, lead dithizonate is extracted by the organic reagent and colors the latter red. The optical density of the extract obtained is measured on a photocolorimeter or on a spectrophotometer. The amount of lead is found by means of a calibration curve prepared by means of standard solutions prepared in the same way as the test solution.

In this way it is possible to separate lead from all elements which interfere with its photometric determination by means of dithizone (in particular from thallium, bismuth, and tin).

For determination of lead in rocks, a finely ground sample was decomposed with a mixture of hydrofluoric and perchloric acids. After removal of the acids, the residue was dissolved in dilute hydrochloric acid. To this solution was added 25 ml of a citrate-bicarbonate solution containing 5-10 mg of sodium diethyldithiocarbamate; this was followed after 15 minutes by 25 ml of a mixture of equal volumes of pentanol and toluene. After shaking for two minutes, the layers being allowed to separate, the lower layer was discarded. The organic layer was washed with 25 ml of twice-distilled water. The lead was extracted from the organic solvent by shaking it twice with 10 ml of a dilute hydrochloric acid solution (1 : 10*). The hydrochloric acid solution was added to an ammoniacal cyanide solution containing dithizone. Lead dithizonate was extracted from this solution with carbon tetrachloride. The lead dithizonate solution was made up to a definite volume (15 ml), after which its optical density was determined on a photocolorimeter. A calibration curve was constructed using solutions of lead in 10 ml of HCl (1 : 10), these solutions being given the same treatment as the test solutions.

In order to assure ourselves of the actual specificity of the method, comparatively large amounts of thallium, bismuth, and tin (100-250 γ) were taken, and extractions carried out under the same conditions as those used for extracting lead. During the re-extraction with dilute hydrochloric acid, complete removal of the elements indicated was achieved.

Results for the determination of lead in rocks by the method just described, agree with the results obtained by the other methods (Table).

Comparative Results for the Determination of Lead by the Various Methods

Sample	Lead found, in %				
	Polarographically			Photometrically	
	After extraction with dithizone solution	After coprecipitation with $BaSO_4$	After heating in the presence of carbon	After extraction with dithizone solution	After extraction as diethyldithiocarbamate
Granodiorite	$1,5\cdot10^{-3}$	$1,6\cdot10^{-3}$	$1,6\cdot10^{-3}$	$1,7\cdot10^{-3}$	$1,6\cdot10^{-3}$
Even grained granodiorite	$1,6\cdot10^{-3}$	$1,5\cdot10^{-3}$	$1,6\cdot10^{-3}$	$1,5\cdot10^{-3}$	$1,6\cdot10^{-3}$
Porphyry, Granite	$3,6\cdot10^{-3}$	$3,1\cdot10^{-3}$	$2,9\cdot10^{-3}$	$3,8\cdot10^{-3}$	$3,4\cdot10^{-3}$
Quartz porphyry	$4,1\cdot10^{-3}$		$3,9\cdot10^{-3}$		
Triandesite	$2,1\cdot10^{-3}$	$2,2\cdot10^{-3}$		$2,2\cdot10^{-3}$	
Feldspar	$1,0\cdot10^{-3}$	$1,0\cdot10^{-3}$		$1,0\cdot10^{-3}$	
» »	$1,4\cdot10^{-3}$		$1,5\cdot10^{-3}$	$1,7\cdot10^{-3}$	$1,5\cdot10^{-3}$
» »	$1,7\cdot10^{-3}$			$1,8\cdot10^{-3}$	$1,8\cdot10^{-3}$

Lead was extracted to the extent of 97%

5. Separation of lead by distillation. Separation of lead by distillation was carried out by heating the test sample in the presence of carbon in a vacuum** or in a nitrogen stream. The test sample, carefully ground with an equal amount by weight of carbon, was heated in a quartz tube. In the first experiment the lead was separated at a temperature of 1050-1100° and a pressure of $10^{-1} - 10^{-2}$ mm Hg, while in the second experiment lead was removed at a temperature of 1100-1150° in a stream of nitrogen. The distillate which condensed on the cooler parts of the tube was washed off with hot nitric acid (1 : 1); this solution was evaporated to dryness. The lead content of the concentrate thus obtained was determined polarographically. Distillation in vacuo took 3-4 hours, while in nitrogen, distillation was carried out for about 8 hours.

Experiments showed that using this technique it is possible to separate 80 to 100% of lead contained in the rock.

The table contains a comparison of the results obtained for the determination of lead in several samples when the various methods for the preliminary separation and final determination of lead were used.

DISCUSSION OF RESULTS

From the experiments described above on the concentration of lead, the following conclusions can be drawn:

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*This solution was prepared by diluting redistilled hydrochloric acid (1 : 1).

**After completing this work we learned that N. Iordanov and L. Kocheva had also carried out separation of lead in a vacuum in the presence of carbon, and with HgS [16].

1. Concentration, based on the direct extraction of lead dithizonate by means of chloroform from a solution obtained by decomposition of the sample, permits the extraction, on an average, of 91% of all the lead in the rock. This technique of concentration by extraction takes less time than those methods based on coprecipitation.

2. Concentration based on coprecipitation of lead with mercury and zinc sulfides does not achieve the desired results: only 60-70% is extracted with mercuric sulfide and 80-90% with zinc sulfide. The drawback of this method is the high degree of contamination of the concentrate – the sulfide precipitate, which acts as a carrier — by other elements present in solution. Finally, this method is coupled with difficulties arising from the possibility of the hydrolysis of certain salts in the weakly acid solutions, and the even greater complexity of the composition of the concentrate following upon this.

3. Extraction of lead by cocrystallization with the sulfates of the alkaline earth elements, coupled with a subsequent final separation of lead by extraction makes it possible to separate 76% of lead, on the average. The method is complicated by the number of operations involved (for example, fusion with soda, filtration), which lengthen the time taken to carry out a determination, and may cause loss of part of the lead.

4. Separation of lead by extraction of lead diethyldithiocarbamate, with subsequent extraction of lead from the organic solvent by means of dilute hydrochloric acid, ensures removal of lead from all the elements interfering with its final photometric determination with dithizone, in particular, from bismuth and thallium. Lead is extracted to the extent of 97%, on an average. It should be pointed out that an appreciable amount of the reagent employed does not require special preliminary purification. All things considered, this method allows one to separate and determine small amounts of lead contained in rocks fairly simply.

5. Concentration of the lead by distillation effected by heating with carbon permits extraction of 80-100% of the lead. The advantage of the method is the possibility of carrying out a comparatively rapid and simple separation of lead, even from comparatively large samples (2-10 g). The drawback of the method is the complexity of the apparatus.

6. Final photometric determination of lead in the form of its dithizonate is sensitive enough, and permits the lead content of the concentrates to be determined with satisfactory accuracy. The advantage of the method is the possibility of determining lead to relatively small samples; its drawback is the use of potassium cyanide.

The polarographic technique permits small amounts of lead, separated from fairly large samples (1-2 g), to be determined comparatively rapidly and with a high degree of accuracy. When this technique is used potassium cyanide can be avoided.

7. The choice of the method to be used for isolating and determining lead in each special case should be made on the basis of the characteristic composition of the test material and the amount of the latter available.

The author wishes to thank Yu. V. Morachevskii for his valuable advice in the course of the work described above.

SUMMARY

Small amounts of lead in rocks have been determined after concentrating the lead by the following techniques: extraction of lead dithizonate or lead diethyldithiocarbamate with organic solvents; coprecipitation of lead sulfide with mercury or zinc sulfide; coprecipitation of lead sulfate with barium sulfate; distilling off the lead by heating the sample with a solid reducing agent (carbon) in a vacuum, or in a stream of nitrogen. The lead separated by these various techniques was finally determined either polarographically or colorimetrically (dithizone).

The advantages and disadvantages of the various methods for concentrating traces of lead are discussed.

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*Translation of Russian – Publisher's note.

**All-Union Geological Scientific Research Institute.

***Russian translation.

****Probably Bulgarian. Transliteration of Russian – B"lg.

AMPEROMETRIC TITRATION OF IRIDIUM USING A ROTATING PLATINUM ELECTRODE

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We established previously [1] that it is possible to obtain clearly defined current-voltage curves for Na_2IrCl_6 on a platinum electrode; this fact has permitted us to use these curves for the amperometric titration of iridium. The amperometric titration method is no less accurate and sensitive than the polarographic method, and is simpler than the latter, while the apparatus used is more readily available. Oxidation–reduction, and precipitation reactions can be used as a basis for amperometric titration. Since no reagents have hitherto been found which precipitate iridium completely enough, we only used the reduction of Ir^{IV} as a basis for amperometric titration. Reactions of this type proceed quickly and the titration curves obtained have a clearly defined inflection at the equivalence point. Hydroquinone and ascorbic acid were chosen as the titrating reagents. These reducing agents have been successfully used by a number of workers [2-6] for the titrimetric determination of comparatively large amounts of iridium. Other reducing agents which have been described in the literature,such as $FeSO_4$, $K_4Fe(CH)_6$, KI and $TlCl_3$, cannot be used — the first and second, because trivalent iron is reduced at the potential at which iridium is titrated, and the last because of insufficient selectivity. Titration was carried out on the basis of the cathodic wave for the reduction of Ir^{IV} at a potential corresponding to the limiting current. Titration on the basis of the anodic waves of hydroquinone or ascorbic acid is impossible, since, as titration proceeds, the trivalent iridium formed gives an oxidation wave [1] which fuses with the oxidation wave of hydroquinone or ascorbic acid.

Titration was carried out on the apparatus described in [1]. The indicator electrode was a rotating platinum electrode 5-7 mm long and 0.5 mm in diameter, while the reference electrode was a saturated calomel electrode. The electrode was rotated at the rate of 800-1000 revolutions/minute. Measurements were carried out by means of the SGM-8 "Geologorazvedka" polarograph with a galvanometer whose sensitivity was $2.32 \times$ $\times 10^{-9}$ amps./mm/m. The titrant was added from a microburet with 0.02 ml scale divisions. The volume of the solution being titrated, during titration of tenths and hundredths of a milligram was 10 ml, while for the titration of milligram amounts of volume was 30 ml. The supporting electrolyte was 0.1 N NaCl. The Na_2IrCl_6 was prepared in the usual way; the solution was standardized gravimetrically; the concentrations used were approximately 1 mg/ml and 0.1 mg/ml. The solutions of hydroquinone and ascorbic acid used were approximately 0.025, 0.005, and 0.0005 N (1 ml of solution corresponded respectively to 5.0, 1.0, and 0.1 mg of iridium). Solutions of both reagents were prepared in twice-distilled water, 2 ml of HCl being added per ml of solution ; the solutions were stored in dark-colored flasks. Under these conditions the normality of the hydroquinone solutions remained constant over 2-3 weeks, while that of the ascorbic acid solutions was,unfortunately, only constant for 2-3 days. Stabilization of the ascorbic solutions by addition of formic acid and Complexon III, as carried out by other workers [7], was impossible in our case, since these compounds readily reduce Ir^{IV} to Ir^{III}. Hydroquinone solutions were standardized visually by titration with dichromate (using diphenylamine as indicator). Ascorbic acid solutions were standardized by visual titration with trivalent iron (in the presence of SCH^-) or by amperometric titration with a standard solution of Ir^{IV}; standardization was carried out daily.

Titration of iridium with dichromate. In acid media, iridium is very rapidly reduced by hydroquinone at room temperature. Hydroquinone is not reduced on the rotating platinum electrode; on the contrary, it gives an anodic oxidation wave with a limiting current starting at approximately +0.55 volt (saturated calomel electrode). Quadrivalent iridium gives a reduction wave with $E_{1/2}$ = +0.73 volt (Fig. 1). As a result of this, the amperometric curves obtained during the titration of quadrivalent iridium with hydroquinone over the range +0.4—0.5 volt have an L-shape. Changes in the pH of the solution over the range 0.3 to 3.0 do not affect the titration results. Titration was usually carried out in the presence of HCl (pH 1.5) in 0.1 N NaCl. Titration results for various amounts of iridium (from 1.5×10^{-3} to 1×10^{-5} M/liter) (Table 1) indicate that the determination can be carried out with satisfactory accuracy. The mean relative reproducibility of the results amounts to 1-2%. Titration curves for solutions containing $10^{-5} - 5 \times 10^{-4}$ M iridium are in the form of two intersecting straight lines, while titration curves for more concentrated solutions have an initial small horizontal section (Fig. 2).

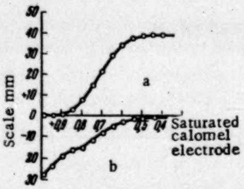

Fig. 1. Current-voltage curves for Na_2IrCl_6 and hydroquinone: a) 6 × $\times 10^{-4}$ M Na_2IrCl_6 in 0.1 N NaCl; b) 2.5×10^{-4} M hydroquinone in 0.1 N NaCl.

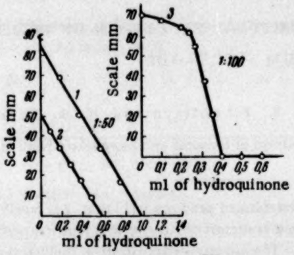

Fig. 2. Titration curves of Ir^{IV} with hydroquinone: 1) 1 mg Ir (5.2×10^{-4} M); 2) 0.6 mg Ir (3.1×10^{-4} M); 3) 2 mg Ir (1.4×10^{-3} M). For curves 1 and 2, 1 ml of hydroquinone solution corresponds to 1 mg Ir, while for curve 3, 1 ml of hydroquinone corresponds to 5 mg Ir.

Rhodium present in any amount does not interfere with the titration of iridium with hydroquinone, since rhodium is reduced on the platinum electrode at more negative potentials, and, moreover, it is not titrated by hydroquinone. For the same reason Pt, Pd, Cu, Ni, Se, and Te do not interfere. On the other hand, Au^{III} whose half-wave potential is similar to that of Ir^{IV} is also reduced by hydroquinone, and accordingly interferes with determination of iridium. In the presence of appreciable amounts of quadrivalent ruthenium, establish-

TABLE 1

Titration of Na_2IrCl_6 with Hydroquinone

Ir taken, mg	Ir concentration, mole/liter	Volume of solution, ml	Normality of hydroquinone solution, N	Ir found, mg	Absolute error, mg	Relative error, %
8,57	$1,5\cdot10^{-3}$	30	0,005	8,40	—0,17	—1,9
4,20	$0,7\cdot10^{-3}$	30	0,005	4,27	+0,070	+1,6
2,14	$1,1\cdot10^{-3}$	10	0,005	2,17	+0,030	+1,4
1,515	$6,2\cdot10^{-4}$	10	0,005	1,525	+0,010	+0,7
0,918	$4,7\cdot10^{-4}$	10	0,005	0,920	+0,020	+2,2
0,850	$4,4\cdot10^{-4}$	10	0,005	0,870	+0,020	+2,3
0,500	$2,6\cdot10^{-4}$	10	0,005	0,510	+0,010	+2,0
0,200	$1,0\cdot10^{-4}$	10	0,005	0,200	0	0
0,095	$4,6\cdot10^{-5}$	10	0,0005	0,094	—0,001	—1,0
0,060	$3,1\cdot10^{-5}$	10	0,0005	0,059	—0,001	—1,6
0,050	$2,6\cdot10^{-5}$	10	0,0005	0,049	—0,001	—2,0
0,035	$1,8\cdot10^{-5}$	10	0,0005	0,038	—0,003	+8,5
0,020	$1,0\cdot10^{-5}$	10	0,0005	0,020	0	0
0,015	$7,7\cdot10^{-4}$	10	0,0005	0,018	+0,003	+20,0

ment of the equivalence point from the titration curves is complicated by the fact that ruthenium is partially reduced by hydroquinone. After treating solutions containing Ir^{IV} and Ru^{IV} with aqua regia, and subsequent evaporation to dryness with hydrochloric acid in the presence of sodium chloride, ruthenium is converted into a compound which is not titrated by hydroquinone, but gives instead a considerable reduction current at +0.4 volt. By preparing the solutions in this way it is possible to determine iridium fairly accurately in the presence of as much as 20-25 times its amount of ruthenium. It should be noted that even small amounts of ruthenium interfere with the polarographic determination of iridium.

Determination of iridium in the presence of small amounts of iron is complicated by the fact that Fe^{III} gives a reduction wave close to that of Ir^{IV} on the platinum electrode. Interference from iron can, however, be overcome by addition of phosphoric acid. When this is done, iridium can be determined in the presence of even as much as 100 times its own amount of iron.

Results for the titration of iridium in the presence of various metals are given in Table 2.

TABLE 2

Titration of Iridium with Hydroquinone in the Presence of Other Metals

Ir taken, mg	Ir : Me	Amount of metal, mg									Ir found, mg
		Pt	Pd	Rh	Ru	Cu	Ni	Fe	Se	Te	
0,060	1:10	—	—	0,6	—	—	—	—	—	—	0,058
0,060	1:200	—	—	12,0	—	—	—	—	—	—	0,060
0,050	1:100	—	5,0	—	—	—	—	—	—	—	0,050
0,050	1:200	—	10,0	—	—	—	—	—	—	—	0,049
0,020	1:20	0,4	—	—	—	—	—	—	—	—	0,020
0,020	1:200	4,0	—	—	—	—	—	—	—	—	0,020
0,045	~1:1	—	—	—	0,05	—	—	—	—	—	0,046
0,045	~1:10	—	—	—	0,50	—	—	—	—	—	Determination impossible
0,060	1:2	—	—	—	0,12*	—	—	—	—	—	0,060
0,060	1:20	—	—	—	1,20*	—	—	—	—	—	0,062
0,060	1:50	—	—	—	3,00*	—	—	—	—	—	0,070
0,060	1:20	—	—	—	—	1,2	—	—	—	—	0,059
0,060	1:10	—	—	—	—	—	0,6	—	—	—	0,061
0,050	1:1	—	—	—	—	—	—	0,05	—	—	0,050
0,050	1:10	—	—	—	—	—	—	0,50	—	—	0,057
0,060	1:60	—	—	—	—	—	—	—	3,0	—	0,063
0,050	1:100	—	—	—	—	—	—	—	—	5,0	0,052
0,60	—	2,0	0,5	6,0	3,0*	—	—	—	—	—	0,60
0,60	—	3,0	0,5	3,0	1,5*	2,0	—	—	0,3	0,5	0,61
0,80	—	—	—	7,0	3,0*	5,0	—	0,5	3,0	2,0	0,78

*Ru^{IV} solutions were treated with aqua regia and then twice evaporated to dryness with HCl in the presence of NaCl.

Titration of iridium with ascorbic acid. Reduction of Ir^{IV} by ascorbic acid, as already established by Pshenitsyn and Prokof'eva [6], proceeds stoichiometrically at room temperature. Ascorbic acid is oxidized on the platinum electrode to give an anodic wave whose half-wave potential depends on the pH of the solution. At a pH of 1.5 the half-wave potential of ascorbic acid is approximately equal to 0.7-0.8 volt (saturated calomel electrode)(Fig. 3). The curves obtained during the amperometric titration of iridium with ascorbic acid at E = 0.4-0.5 volt (saturated calomel electrode) (Fig. 4) are similar in shape to those obtained during titration of iridium with hydroquinone (Fig. 2). Since the oxidation-reduction potential of ascorbic acid increases appreciably with increasing acidity of the medium, experiments were carried out on the titration of Na_2IrCl_6 at HCl concentrations ranging from 10^{-3} to 10 N. It was found that, on changing the acidity, the titration results did not change since the oxidation-reduction potential of $IrCl_6^{2-}/IrCl_6^{3-}$ also increase. Nevertheless, in a strongly acid medium (5-10 N HCl) the reduction of iridium was slowed down, and a titration took a very long time. Subsequent experiments were carried out at a pH of 1.5. Table 3 contains the results for the titration of various amounts of iridium with ascorbic acid.

The mean relative reproducibility during titration of hundredths of a milligram of iridium (> 10^{-5} M) is approximately 4%, while for the titration of tenths of a milligram of iridium (> 10^{-4} M) it is 2-3%. The relative experimental error varies from 1 to 5%, while for the titration of very small amounts (1 x 10^{-5} M and less) it amounts to 10-15%. The smallest amount of iridium which can be determined when the volume of the solution is 10 ml is 0.02 mg. Those metals which do not interfere during titration of iridium with hydroquinone, do not interfere with titrations involving ascorbic acid as titrant. Gold, ruthenium, and iron interfere. For preventing interference from ruthenium, the same technique as that used for titration with hydroquinone was adopted. This technique permitted determination of iridium in the presence of as much as 50 times its amount of ruthenium. Gallai, Tiptsova, and Peshkova [7] during titration of Ce^{IV} with ascorbic acid, established that as a consequence of the fact that there is hardly any reduction of Fe^{III} by ascorbic acid in 2 N H_2SO_4, iron does not interfere with determination of cerium.

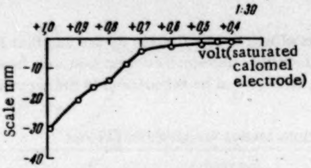

Fig. 3. Current-voltage curves for 2.5 x 10^{-4} M ascorbic acid. Supporting electrolyte 0.1 N NaCl, pH 1.5.

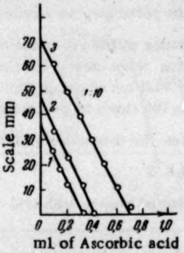

Fig. 4. Titration curves for iridium with ascorbic acid: 1) 0.03 mg Ir (1.5 x 10^{-5} M); 2) 0.4 mg Ir (2 x 10^{-5} M); 3) 0.07 mg Ir (3.6 x 10^{-5} M). (1 ml corresponds to 0.1 mg Ir).

TABLE 3

Titration of Na_2IrCl_6 with Ascorbic Acid

Ir taken, mg	Concentration, mole/liter	Ascorbic acid concentration, N	Ir found, mg.	Absolute error, mg	Relative error, %
9,40	$4,9\cdot10^{-3}$	0,025 N	9,50	+0,10	+1,0
8,10	$4,2\cdot10^{-3}$	0,025 N	8,25	+0,15	+1,8
6,30	$3,3\cdot10^{-3}$	0,025 N	6,50	+0,20	+3,2
1,00	$5,2\cdot10^{-4}$	0,005 N	1,03	+0,03	+3,0
0,60	$3,1\cdot10^{-4}$	0,005 N	0,60	0	0
0,50	$2,6\cdot10^{-4}$	0,005 N	0,50	0	0
0,20	$1,0\cdot10^{-4}$	0,005 N	0,19	−0,01	−5,0
0,07	$3,6\cdot10^{-5}$	0,0005N	0,073	+0,003	+4,3
0,05	$2,6\cdot10^{-5}$	0,0005N	0,050	0	0
0,03	$1,5\cdot10^{-5}$	0,0005N	0,032	+0,002	+6,6
0,02	$1,0\cdot10^{-5}$	0,0005N	0,023	+0,003	+15,0

Since ascorbic acid reduces Ir^{IV} even in very acid media, we tried to use this fact for the determination of iridium in the presence of iron. It is clear from the results given in Table 4 that when titration is carried out in 7-10 N HCl, iron present to the extent of 100 times the iridium does not interfere with the titration of the latter. In such acid media, however, titration is slowed down. Moreover, the diffusion current of iron only disappears completely in 10 N HCl. Accordingly, another method of preventing interference from Fe^{III} – complexing it as a phosphate complex by addition of 2 ml of H_3PO_4 (60%) – is more convenient; when this technique is used the diffusion current of Fe^{III} disappears completely, and, moreover, the rate of reduction of Ir^{IV} is not slowed down.

TABLE 4

Titration of Ir^{IV} in the Presence of Fe^{III} at Various Acidities of the Medium (0.50 mg Ir was taken)

Fe taken, mg	HCl concentration, N	Ir found, mg	Residual current, mm
5.0	10^{-3}	0.66	20
5.0	5	0.54	10
5.0	7	0.49	5
5.0	10	0.51	–
50.0	7	0.48	15.0

The results obtained (Table 5) indicate that it is possible to titrate Ir^{IV} with ascorbic acid in the presence of Rh, Pt, Pd, Ru (for ratios of Ir : Ru not greater than 1 : 50), Cu, Ni, Pb, Se, Te, and Fe (after addition of H_3PO_4).

TABLE 5

Titration of Iridium with Ascorbic Acid in the Presence of Other Metals

Ir taken, mg	Ir:Me	Amount of the other metal present as an impurity, mg										Ir found, mg
		Pt	Pd	Ph	Ru*	Cu	Ni	Pb	Fe	Se	Te	
0,50	1:10	5,0	—	—	—	—	—	—	—	—	—	0,52
0,50	1:100	50,0	—	—	—	—	—	—	—	—	—	0,51
0,60	1:10	—	6,0	—	—	—	—	—	—	—	—	0,62
0,60	1:100	—	60,0	—	—	—	—	—	—	—	—	0,62
0,60	1:10	—	—	6,0	—	—	—	—	—	—	—	0,60
0,60	1:100	—	—	60,0	—	—	—	—	—	—	—	0,62
0,50	1:10	—	—	—	5,0	—	—	—	—	—	—	0,51
0,50	1:90	—	—	—	45,0	—	—	—	—	—	—	0,49
0,50	1:20	—	—	—	—	10,0	—	—	—	—	—	0,50
0,50	1:20	—	—	—	—	—	10,0	—	—	—	—	0,52
0,50	1:20	—	—	—	—	—	—	10,0	—	—	—	0,50
0,066	1:10	—	—	—	—	—	—	—	0,6	—	—	0,066
0,066	1:100	—	—	—	—	—	—	—	6,0	—	—	0,066
0,40	1:25	—	—	—	—	—	—	—	—	10,0	—	0,41
0,40	1:25	—	—	—	—	—	—	—	—	—	10,0	0,40
0,70	—	3,0	3,0	7,0	7,0	—	—	—	—	—	—	0,73
0,80	—	3,0	3,0	5,0	3,0	10,0	3,0	—	5,0	1,0	0,5	0,84

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*Ru^{IV} solutions were treated with aqua regia and then twice evaporated to dryness with HCl in the presence of NaCl.

SUMMARY

It has been established that it is possible to titrate small amounts of Ir^{IV} (10^{-5} – 10^{-3} M) amperometrically with hydroquinone and ascorbic acid respectively, in the presence of Rh, Pt, Pd, Cu, Ni, Pb, Se, and Te. Conditions have been found for the titration of iridium in the presence of Ru^{IV} and Fe^{III}.

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POTENTIOMETRIC DETERMINATION OF PHOSPHATE IONS

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The aim of the work described in the present article was to develop a rapid and accurate method for the potentiometric titration of phosphate ions.

We used a mercury electrode while the titrant used was a solution of mercuric nitrate; a saturated calomel half element was used as the reference electrode in the normal type of compensation setup. The indicator mercury electrode that was constructed had a number of advantages over mercury electrodes which have been suggested hitherto [1, 2]. The titration beaker 3 had an offshoot (Fig. 1), which was filled with mercury, and a tap 5 which served for pouring off the liquid which had been titrated and for washing the beaker. Contact was established by placing a platinum disc in the mercury, the platinum disc being connected via a wire fused into a glass tube provided with an external lead. The salt bridge was filled with a saturated solution of KCl or KNO_3.

The $Hg(NO_3)_2$ was added in small aliquots, and, towards the equivalence point, in drops.

Potentiometer readings were made every minute (after a constant value of the potential had been reached). A titration curve for phosphates is shown in Fig. 2.

TABLE 1

Results for the Titration of Phosphates with 0.161 N Mercuric Nitrate

PO_4^{3-} taken, mg/liter	PO_4^{3-} found, mg/liter	Error, %
28.40	28.42	+ 0.07
22.14	22.27	+ 0.58
11.01	10.84	− 1.53
5.17	5.06	− 2.12
4.03	3.45	−14.39
2.61	2.08	−20.31

In order to study the accuracy of the method we had developed, PO_4^{3-} ions at various concentrations were potentiometrically titrated with 0.161 N mercuric nitrate.

It is evident from Table 1 that the error increases with decreasing phosphate concentration. For concentrations not less than 5 mg/liter, the accuracy of the potentiometric titration was satisfactory. The reproducibility of the results for potentiometric titration of phosphates was good.

Addition of alcohol to the solution being titrated made it possible to lower the titration error for small amounts of PO_4^{3-} ions, since alcohol, on the one hand, being a surface-active agent, lowers adsorption; while on the other hand, it lowers the solubility of the precipitates [3, 4].

The soil extracts tested often contain colloidal materials; nevertheless, the latter did not interfere with the titration of phosphate ions. Addition of gelatine to the test solution in amounts which were 20-100 times the PO_4^{3-} ions present, had almost no effect on the results. Larger amounts of gelatin (up to 600 mg) gave solutions which were so viscous that titration became difficult.

As noted above, during titration of small amounts of phosphate ions, there was observed a significant shift of the break on the titration curve from the equivalence point. Titration errors could be lowered considerably, and, sometimes even reduced to zero, by carrying out the determination of the phosphate ions by the double addition method. This technique of Shakhkel'dian has been used on several occasions [5-8].

It is clear from Table 2, that during the determination of small amounts of phosphate ions without using the double addition method the experimental error varies from 15.8 to 23.9%, while when this method is adopted the error varies from 0 to 4.7%. Thus, the double addition method is a better method from the point of simplicity and rapidity than the method of applying corrections for titration errors. Many test materials (minerals, soils, natural water) contain, as a rule, large amounts of chloride ions. On addition, however, of chlorides to the test solution in amounts which were 10-100 times that of the PO_4^{3-} ions, the titration results for the phosphate ions did not change; thus chlorides do not interfere with the quantitative determination of PO_4^{3-}. It is possible to carry out successive titration of phosphate and chloride ions. In Fig. 3, is shown the titration curve obtained for a solution containing both chloride and phosphate ions. PO_4^{3-} ions are titrated first and then the chloride ions.

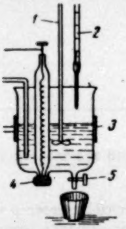

Fig. 1. Mercury indicator electrode: 1) Stirrer; 2) buret containing titrant; 3) titration beaker; 4) mercury indicator electrode; 5) tap for pouring off liquid which has been titrated.

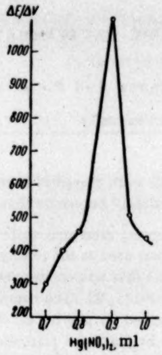

Fig. 2. Potentiometric titration curve for 5.47 mg PO_4^{3-} ions with 0.188 N $Hg(NO_3)_2$.

TABLE 2

Potentiometric Titration of Phosphate Ions using the Double Addition Method

PO_4^{3-} taken, mg	PO_4^{3-} found, mg	Error %	PO_4^{3-} taken, mg	First addition of PO_4^{3-}, mg	$Hg(NO_3)_2$ used for titration, ml	Second addition of PO_4^{3-}, mg	$Hg(NO_3)_2$ used for titration, ml	PO_4^{3-} found, mg	Error, %
4,10	3,45	15,8	4,10	1,37	0,9	23,35	4,6	4,00	2,4
4,10	3,45	15,8	4,10	1,37	0,9	6,84	1,8	4,10	0
4,10	3,45	15,8	4,10	1,37	0,9	17,78	3,7	3,91	4,5
2,73	2,08	23,9	2,73	2,73	0,9	19,35	3,7	2,65	2,9
2,73	2,08	23,9	2,73	2,73	0,9	8,19	1,8	2,73	0
2,73	2,08	23,9	2,73	2,73	0,9	24,62	4,6	2,60	4,7

Titration of solutions containing phosphates can be carried out within a wide pH range of 10 to 3. At pH < 3 in the original solution, the accuracy of the potentiometric titration method decreases because of the increase in solubility of the precipitate of $Hg_3(PO_4)_2$ formed during titration.

Under the conditions we used, Ca^{2+}, Ba^{2+}, Mg^{2+}, and SO_4^{2-} do not interfere.

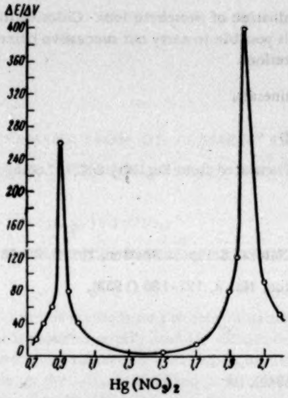

Fig. 3. Potentiometric titration curves for 5.47 mg PO_4^{3-} ions in the presence of 7.16 mg Cl, using 0.188 N $Hg(NO_3)_2$ as titrant.

The method which we had developed for determination of phosphates was checked on samples of minerals (Table 3).

1 g of the mineral was introduced into a conical flask and dissolved in 30 ml of aqua regia by heating and constant agitation of the contents of the flask over a period of 30 minutes. The hot solution was neutralized with 2 N NaOH to a weak alkali reaction; it was then filtered into a 200 ml standard flask; the filtrate was cooled and its volume made up to the mark with distilled water. An aliquot (50 ml) of this solution was transferred to the titration beaker, and titrated with mercuric nitrate solution. When the phosphate content was low the double addition method was used.

The equivalence point during titration was found on addition of 8.10 ml of $Hg(NO_3)_2$ solution. The total PO_4^{3-} content of the sample of mineral was 19.28%.

When the gravimetric method based on precipitation in the form of pyrophosphate (double precipitation) was used, the value found was 19.46%. Accordingly, the potentiometric titration method is as accurate as the gravimetric method, and has the advantages that it is quicker and simpler (an analysis takes 1.5-2 hours).

TABLE 3

Potentiometric Titration of Phosphate Ions in a Mineral Brought Back by the Geological Expedition of the Rostov State University to the Kamenskii Region; the Mineral was Found on the Right Bank of the River Don near Beshenskii ($T_{Hg(NO_3)_2/PO_4^{3-}} = 0.00595$ g)

$Hg(NO_3)_2$ solution used, mg	emf established, millivolts	ΔE	ΔV	$\frac{\Delta E}{\Delta V}$	$Hg(NO_3)_2$ solution used, mg	emf established, millivolts	ΔE	ΔV	$\frac{\Delta E}{\Delta V}$
7,50	476	—	—	—	8,00	502	7	0,05	140
7,60	477	1	0,10	10	5,05	512	10	0,05	200
7,70	479	2	0,10	20	8,10	530	18	0,05	360
7,80	482	3	0,10	30	8,15	540	10	0,05	200
7,85	486	4	0,05	80	8,20	545	5	0,05	100
7,90	490	4	0,05	80	8,30	548	3	0,10	30
7,95	495	5	0,05	100	8,40	551	3	0,10	30

SUMMARY

1. A method involving the use of a mercury indicator electrode has been developed for the potentiometric titration of PO_4^{3-} ions. It was found that with decreasing phosphate concentration the experimental error increased. However, addition of ethanol to the solution being titrated improves the experimental results; this improvement is the result of a decrease in the solubility of the precipitate of $Hg_3(PO_4)_2$.

The double addition method led to a significant decrease in the experimental error during the determination of low concentrations of phosphate ions.

2. The reproducibility of the method is good. Good results can be obtained at a pH of 3-4 and higher.

3. Colloidal materials do not affect the results of the determination of phosphate ions. Chloride ions do not interfere with determination of PO_4^{3-} ions. Furthermore, it is possible to carry out successive titration of PO_4^{3-} and Cl^- ions. Ca^{2+}, Ba^{2+}, Mg^{2+}, and SO_4^{2-} ions do not interfere.

4. Satisfactory results were obtained during the analysis of minerals.

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DETERMINATION OF ELEMENTAL SULFUR BY EXTRACTION WITH CARBON TETRACHLORIDE

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Current methods for the determination of elemental sulfur are fairly time consuming and difficult. The methods most frequently used are extraction of sulfur with carbon disulfide and the sulfite method [1]. In the method where extraction with carbon disulfide is used, the sulfur is weighed after distilling off the carbon disulfide, or the sulfur is oxidized to sulfate which is then precipitated as barium sulfate. This method has a number of technical drawbacks: extraction is carried out in diffused light to prevent decomposition of the carbon disulfide, while the volatility and the high inflammability of this solvent demand great care. Determination of elemental sulfur by this method takes 5-6 hours [1]. When elemental selenium, which is readily soluble in carbon disulfide, is present, it must be removed prior to determination of the sulfur.

The simplest method, from the practical point of view, is the sulfite method which is based on extraction of sulfur with an aqueous solution of sodium sulfite: $Na_2SO_3 + S = Na_2S_2O_3$; the thiosulfate formed is titrated with iodine solution. The sulfite method is inapplicable in the presence of polysulfides, since the latter, like elemental sulfur, interact with sulfite [2]. This method also cannot be used when elemental selenium is present, since selenium dissolves in the sulfite: $Na_2SO_3 + Se = Na_2SO_3Se$.

Water-soluble compounds of arsenic, iron, copper, etc., which react with iodine, also introduce considerable complications into the method for the determination of sulfur.

The cyanide method of Castiloni [3] is less widely used; this method is based on the interaction of elemental sulfur with potassium cyanide in an acetone medium with formation of a thiocyanate: $KCN + S = KSCN$ (when tellurium is present, a tellurocyanate is formed). After removal of acetone by distillation the residue is dissolved in water and the thiocyanate determined argentometrically. Romm [3] used this method for the determination of elemental sulfur in slime from salt lakes, but substituted the argentometric finish by a photometric finish with ferric salts. The method gives good results, the use of potassium cyanide is, however, connected with some disadvantages.

A rapid method based on distilling off the elemental sulfur has been developed by Libina, Miller, and Musakin [2]. The experimental technique involved is simple and permits determination of elemental sulfur in materials containing sulfates, thiosulfates, and polysulfides in the course of 15-20 minutes. This method is inapplicable when the test material contains readily distilled compounds of mercury, and arsenic.

Details of a polarographic method for determining elemental sulfur have also been published [4], however, this method has only been worked out for the analysis of petroleum (elemental sulfur content of 10^{-2} — 10^{-4}%). The polarographic method is not applicable when the elemental sulfur content is high.

Materials which we have had to analyze contained large amounts of the sulfides of mercury and other metals, arsenic and antimony oxides, and various sulfur-containing compounds: thiosulfates, sulfates, sulfites, and polythionates. The elemental-sulfur content of these materials varied from 2-10%. Our problem was therefore to develop a convenient method for the determination of elemental sulfur in such materials. The most suitable technique for this purpose is extraction of elemental sulfur with some organic solvent. In addition to carbon disulfide, elemental sulfur also dissolves in benzene, toluene, chloroform, and carbon tetrachloride. The solubility of elemental sulfur in carbon tetrachloride is about 2% at 50° [5].

Carbon tetrachloride has a number of advantages over carbon disulfide as an extractant for sulfur. The considerably higher boiling point of carbon tetrachloride (76°) as compared with that of carbon disulfide permits extraction to be carried out more rapidly. There is no need to observe the precautions which are necessary on account of the inflammability of carbon disulfide. For the determination of large amounts of sulfur extraction can be carried out directly in a conical flask fitted with an air condenser.

Results for the determination of elemental sulfur in synthetic mixtures and in rocks, by the sulfite method and by extraction with carbon tetrachloride are given in Tables 1 and 2.

TABLE 1

Determination of Elemental Sulfur in Synthetic Mixtures Made up from Finely Ground Silicate Rock and Elemental Sulfur

Sample wt., g	Elemental sulfur content, %				
	taken	found			
		by the sulfite method [1]		by extraction with CCl_4	
5,0	0,10	0,10	0,11	0,10	0,10
5,0	0,10	0,10	0,09	0,10	0,10
5,0	0,25	0,25	0,24	0,24	0,26
5,0	0,50	0,48	0,49	0,48	0,49
2,0	0,75	0,73	0,74	0,72	0,73
2,0	1,00	1,03	1,02	1,02	1,02
2,0	1,00	1,01	1,00	0,98	1,02
1,0	2,50	2,48	2,52	2,50	2,56
1,0	5,00	5,07	5,04	5,09	4,98
1,0	5,00	5,07	5,09	5,08	5,07

TABLE 2

Determination of Elemental Sulfur in Rocks

Sulfur found, %					Relative error, %
by the sulfite method	by extraction with CCl_4				
				Mean	
0,74	0,70	0,76	0,75	0,74	—
1,42	1,40	1,46	1,48	1,44	+1,4
0,49	0,54	0,52	0,52	0,53	+8,2
2,33	2,25	2,26	2,30	2,27	—2,4
0,90	0,85	0,87	0,84	0,85	—5,5

Having obtained consistent results for the determination of elemental sulfur in synthetic mixtures and rocks, we determined sulfur in materials containing oxides, sulfates, sulfites, and other salts of sulfur-containing acids.

Analytical results were controlled by carrying out the determinations on samples of varying weights. The results obtained are given in Table 3.

TABLE 3

Determination of Elemental Sulfur in Materials Containing Oxides, Sulfides, Sulfates, and Other Compounds

Elemental sulfur found, %					Mean content, %
sample weight, g					
0,5	1,0	1,0	2,0	2,0	
1,80	1,79	1,74	1,82	1,80	1,79
2,71	2,69	2,68	2,72	2,70	2,70
6,02	5,98	5,96	6,14	6,07	6,03
10,24	10,30	10,21	10,37	10,12	10,24

These results show that it is possible to determine elemental sulfur by the suggested method in complex materials.

The presence of small amounts of elemental selenium and tellurium (up to 0.5%) in the test materials does not affect the experimental results for sulfur.

Experimental procedure for the determination of elemental sulfur. For sulfur contents not greater than 0.1%, 0.5-2 g of test material is taken for determination of elemental sulfur; while for lower sulfur contents, 2-5 g of test material is taken. The sample is prepared for analysis in the same way as that described for extraction with carbon disulfide [1]. For sulfur contents less than 0.1%, the sulfur is extracted with carbon tetrachloride in a Soxhlet apparatus for 1-1.5 hours. After extraction is complete, the flask with the extracted sulfur is disconnected from the Soxhlet apparatus and the carbon tetrachloride distilled off by heating the flask on a naked flame (the carbon tetrachloride is distilled off under a forced draught). When only 2-3 ml of carbon tetrachloride is left in the flask, the rest is evaporated off on a sand bath heated to 75-80° and covered with an asbestos board. The crystalline sulfur formed after evaporationg the carbon tetrachloride is then weighed.

For elemental sulfur contents greater than 0.1-0.2% the procedure can be simplified considerably (in such cases extraction can be carried out in a conical flask fitted with an air condenser rather than in a Soxhlet).

An aliquot is placed in a 100 ml conical flask and 50 ml of carbon tetrachloride added; the flask is fitted with an air condenser and the whole heated at 50-60° on a sand bath covered with an asbestos sheet, or on an asbestos grid for 1 hour. At the end of this time the reflux condenser is disconnected and the solution obtained filtered into another 100 ml flask through a fine paper filter by decantation. In order to prevent sulfur crystallizing out during filtration, funnel and flask should be heated beforehand to 45-50°. The residue from which the solution has been decanted is extracted again, by adding 10 ml of carbon tetrachloride and heating for 5-10 minutes at 50-60°. This solution in turn is poured onto the filter. The filter is washed with two lots of 3-5 ml of carbon tetrachloride heated to 50°. All the solutions are combined. The carbon tetrachloride is then evaporated off (under a forced draught) as indicated above. The sulfur is finally weighed.

When bitumen or some other organic material is present, the elemental sulfur is determined by the sulfite method after distilling off the solvent.

SUMMARY

A simple method has been developed for the determination of elemental sulfur by extraction with carbon tetrachloride; the method is applicable to the determination of sulfur in materials which are difficult to analyze by the methods suggested earlier. The method has been tested on rocks and other materials containing from 0.5 to 10% of elemental sulfur.

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CHEMICOSPECTROGRAPHIC ANALYSIS OF METALLIC BERYLLIUM AND BERYLLIUM OXIDE OF HIGH PURITY

A. G. Karabash, Sh. I. Peizulaev, R. L. Slyusareva, and V. M. Lipatova

Several monographs have been devoted to the chemistry and analytical chemistry of beryllium [1-3]. Chemical methods for the analysis of metallic beryllium and its compounds for the amount of impurities contained in them have been described in a number of papers [4-8]. A bibliography devoted to this question has been given in a special review [8]. Most of the chemical techniques specify determination of the elements in separate aliquots. In one textbook [4] methods are given for the determination of impurities in pure beryllium; of these impurities Fe, Al, Si, and BeO are determined photometrically. Methods have also been published for the direct spectrographic determination of impurities in beryllium [9-10]. The evaporation method has been adopted for the spectrographic determination of boron present as an impurity in beryllium, and the possibility has been demonstrated of determining some other impurities by this method [11].

The chemicospectrographic method of analysis described below is designed for controlling high purity beryllium and beryllium oxide

The chemicospectrographic method permits simultaneous determination of the following 24 elements present as impurities: Mg, Ca, Ba, Al, Ti, V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Sn, Pb, Sb, Bi, Ga, In, Tl, Te. Sodium is determined separately on a glass spectrograph.

Concentration of impurities is effected by removal of beryllium by extraction in the form of its basic acetate $Be_4O(CH_3COO)_6$ with chloroform. Basic beryllium acetate has some very characteristic properties [1,2]. It is fairly stable to the action of many inorganic reagents (water, hydrochloric acid) and readily dissolves in acetic acid, chloroform, nitrobenzene, benzene, toluene, benzine, kerosene, acetone, carbon disulfide, carbon tetrachloride, etc.. The characteristic properties of beryllium acetate, coupled with its covalent structure [12] are responsible for the high selectivity of its extraction separation. The solubility of basic beryllium acetate in chloroform is 50 g per 100 ml of $CHCl_3$, while the acetates of the metals being determined in beryllium are almost insoluble. There are published references to the use of basic beryllium acetate for separating beryllium and aluminum, beryllium and iron [13-14], and also for the preparation of pure standard solutions of beryllium and pure beryllium oxide; the techniques used in these instances were extraction of the basic acetate by organic solvents (carbon tetrachloride, toluene, or xylene) [15] and also sublimation [16-18].

In the work described here a study was made of the behavior of the 24 elements mentioned above, during extraction of basic beryllium acetate with chloroform.

For extracting the impurities, basic beryllium acetate was dissolved in chloroform, and the chloroform solution washed three times with hydrochloric acid (4 N) in a separating funnel. During this operation the impurities were quantitatively transferred into the hydrochloric wash liquor together with a small amount of beryllium (about 1/20 of the original sample taken).

Completeness of the extraction of the impurities into the concentrate during chloroform extraction of basic beryllium acetate was tested in experiments with synthetic mixtures of salts. Impurity elements in amounts ranging from $10^{-3} - 10^{-5}\%$ with respect to beryllium were added to spectrographically pure beryllium acetate. The mixture was treated and extraction carried out under the conditions used in the method developed. Each phase was analyzed — the hydrochloric wash liquor and the chloroform extract — by the most sensitive chemical and spectrographic methods. On the basis of a large number of experiments, mean values of the percentage extraction of traces of the elements into the concentrate (from 85-100%) were found. These values were confirmed in experiments with synthetic mixtures, and also during the analysis of metallic beryllium and beryllium oxide — by checking on the purity of the basic acetate after the chloroform extraction.

In the case of Cd, Cu, Co, Sb, Ag, Fe, Ca, Mn, Cr, Mo, Sn, Zn, In, Na, completeness of extraction was also checked by means of radioactive indicators.

From the hydrochloric acid wash liquor into which part of the beryllium had passed (about 1/10 of the original aliquot) as well as all the impurities, a powdered concentrate of the impurities was prepared. The basis of this concentrate was beryllium oxide in the glass-like form. The latter was prepared as follows: a solution of beryllium nitrate was evaporated to a sirupy state when beryllium hydroxide was precipitated by addition of excess 25% ammonia solution. The thick paste of beryllium hydroxide was dried and calcined until the ammonium nitrate had been completely decomposed. Decomposition of NH_4NO_3 (at 200°) is preceded by its fusion which starts at 165°, so that formation of beryllium oxide takes place under these conditions in the presence of molten ammonium nitrate. The oxide prepared in this way is a dense, granular powder having the appearance of large transparent glass-like grains with a strong luster; it differs sharply from the usual dust-like beryllium oxide (Fig. 1). X-ray structural studies* of the glass-like beryllium oxide showed that it has a hexagonal crystalline lattice of the Wurtzite type which is characteristic of the usual type of BeO, but it differs from the latter in having appreciably smaller crystal dimensions which approximate to those of colloidal particles; this determines its glass-like character. The bulk density of the glass-like oxide is considerably greater than that of the usual, dust-like BeO (twice that of the usual oxide calcined at 1000° and 5 times that of the ordinary partially hydrated oxide). This means that it is possible to pack more of the oxide in the electrode, and this accordingly increases the sensitivity of the spectrographic determinations. The glass-like oxide powder does not raise dust when it is scattered, and it is readily loaded into the crater in the carbon electrode.

Fig. 1. Microphotographs of beryllium oxide: a) Beryllium oxide prepared from the nitrate by calcining at 1000° (dust-form); b) glass-like oxide prepared by the method developed, and used as a basis for spectrographic analysis.

An unenriched sample was prepared at the same time as the chemical concentrate of impurities. Preparation of the unenriched sample consisted of converting it into beryllium oxide in the glass-like form, this being identical with the final stage of the preparation of the concentrate of the impurities. The spectra of the concentrate of the impurities and of the unenriched sample were then photographed together; this enabled the range of concentrations determined to be extended, and to cover the concentration range 1×10^{-1} to 1×10^{-6}%.

The standards for spectrographic analysis were prepared by adding known amounts of standard solutions of the impurity elements to a solution of spectrographically pure beryllium nitrate, and then preparing the glass-like beryllium oxide from the resultant solution.

For controlling the purity of less pure samples, where there is no need for chemical concentration, it is possible to carry out a direct spectrographical analysis of the unenriched samples using the same standards.

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*X-ray structural investigations were carried out by E. S. Makarov.

The sensitivity of the determination of impurities when preliminary concentration is not used is 10^{-3} — 10^{-4}%, while when concentration is used the sensitivity is 10^{-4} — 10^{-5}% (Table 1).

a. Preparation of the chemical concentrate of impurities. 2 g of beryllium (or 5.6 g of beryllium oxide) is dissolved in 90 ml of 6 N HCl plus 10 ml of 14 N HNO_3 contained in a quartz beaker, and the solution evaporated to a sirupy consistency. By a three-stage evaporation with nitric acid (50 ml the first time and 20 ml each the second and third times) to dryness, beryllium nitrate is obtained. Concentrated ammonia is then added to precipitate beryllium hydroxide in the form of a paste; the latter is dried and then calcined, the temperature being brought up slowly to 250-300°. The oxide obtained is dissolved in 100 ml glacial acetic acid, and, after evaporating the solution to dryness, basic beryllium acetate is obtained.

When beryllium oxide which has been calcined at a temperature not higher than 600° is to be analyzed, it can be dissolved directly in glacial acetic acid; after evaporation of the solution thus obtained basic beryllium acetate is prepared.

The basic beryllium acetate is dissolved in 100 ml chloroform. The chloroform solution is washed three times in a separating funnel with 4 N hydrochloric acid; the first time with 30-40 ml of the acid, the second and third times with 20 ml. The hydrochloric acid wash liquors are evaporated in a quartz basin preliminarily heated to 500° and weighed. The sirupy solution is treated three times with nitric acid (first 8 ml and then two lots of 3 ml), the mixture being evaporated each time to a sirupy state. Beryllium hydroxide is precipitated with concentrated ammonia, and the paste of hydroxide thus formed, dried and calcined, the temperature being gradually taken up to 300°. After removal of the ammonium nitrate the mass is calcined for a further half-hour at 500°. The residue is weighed and the enrichment coefficient of the impurity in the concentrate is calcined; this coefficient is equal to the ratio of the original aliquot (in terms of BeO) to the amount of concentrate obtained. Usually, the weight of the concentrate is about 100 mg — in terms of the metal — i.e., the enrichment coefficient is 20-25.

TABLE 1

Analytical Lines and the Sensitivity of Determination of Impurity-Elements in Beryllium

Element	Sensitivity (as a % of metallic Be)		Analytical line, A	Element	Sensitivity (as a % of metallic Be)		Analytical line, A
	during analysis without enrichment	during analysis of the conc. of impur. K-20			during analysis without enrichment	during analysis of the conc. of impur. K-20	
Mg*	$3 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	2802,7	Ag	$3 \cdot 10^{-4}$	$2 \cdot 10^{-5}$	3280,7
Ca*	$2 \cdot 10^{-3}$	$3 \cdot 10^{-4}$	4226,7	Zn	$1 \cdot 10^{-3}$	$5 \cdot 10^{-4}$	3345,0
Ba	$3 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	4934,1;2335,3	Cd	$1 \cdot 10^{-4}$	$5 \cdot 10^{-6}$	2288.0
Al*	$2 \cdot 10^{-3}$	$3 \cdot 10^{-4}$	3082,2	Sn	$2 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	2840,0
Ti	$3 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	3349,0	Pb	$2 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	2833,1
V	$1 \cdot 10^{-3}$	$5 \cdot 10^{-5}$	3184,0;2688,0	Sb	$3 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	2598,1
Cr	$1 \cdot 10^{-3}$	$5 \cdot 10^{-5}$	2835,6	Bi	$1 \cdot 10^{-3}$	$5 \cdot 10^{-5}$	3067,7
Mo	$2 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	2816,2	Te	$3 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	2385,8
Mn	$2 \cdot 10^{-4}$	$1 \cdot 10^{-5}$	2576,1	Ga	$1 \cdot 10^{-3}$	$5 \cdot 10^{-5}$	2874,2
Fe*	$1 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	2599,4	In	$3 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	3256,1
Co	$2 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	3412,6	Tl	$3 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	2767,9
Ni	$2 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	3050,8	Na*	$2 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	5890,0
Cu*	$2 \cdot 10^{-4}$	$3 \cdot 10^{-5}$	3247,5				

At the same time a blank is carried out in which all the reagents are used. The blank is carried out by adding to the hydrochloric acid solution obtained during the extraction, a solution of spectrographically pure beryllium nitrate in an amount corresponding to 100 mg of Be, this serves as the basis for spectrographical analysis.

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*The sensitivity indicated for the determination of Na, Mg, Ca, Al, Fe, and Cu takes into account their possible content in the control experiment.

b. Preparation of the unenriched sample. 0.2 g of metal (or 0.56 g of the oxide) is dissolved in 10 ml of 6 N HCl plus 1 ml of 14 N HNO_3 contained in a quartz basin. The solution obtained is evaporated to a sirupy state, and by treatment with three lots of nitric acid (8 ml, 3 ml, 3 ml) beryllium nitrate is obtained. When beryllium oxide which has not been heated below 1000° is to be analyzed, it can be dissolved directly in nitric acid. Beryllium hydroxide is precipitated as a paste by addition of concentrated ammonia, the hydroxides are then dried and finally calcined, the temperature being gradually taken up to 300°; it is finally heated for half an hour at 500°. The glass-like beryllium oxide is ground up in a quartz mortar and pestle and is then ready for spectrographic analysis.

In order to carry out a blank, spectrographically pure beryllium oxide (or beryllium nitrate) is subjected to the same operations, the same reagents being used as for the sample.

The water, hydrochloric, nitric, and acetic acids used for the work are purified by distillation in quartz apparatus and stored in quartz flasks. Ammonia solution (about 25%) is prepared by saturating twice-distilled water with ammonia by diffusion. For this purpose, the distilled water contained in a quartz flask is placed in a desiccator, in which is also placed a concentrated solution of reagent ammonia to which lumps of NaOH have been added. Quartz beakers, basins and rods are used.

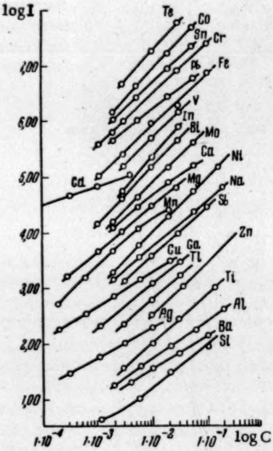

Fig. 2. Calibration curves for the determination of impurities in beryllium. The curves are shifted arbitrarily along the ordinate to avoid intersection.

c. Spectrographic determination of impurities. The spectra of the concentrate of the impurities, sample without enrichment, control tests, and standards are all photographed on the same photographic plate. 24 impurity elements can be determined from one spectrogram. Sodium is determined independently in a separate series of standards on a glass spectrograph. The carbon electrodes are fired in a dc arc at a current strength of 12 amps. for 15 seconds in order to purify them from accidental contamination. The lower electrode is a carbon rod with a crater 4 mm in diameter and 6 mm deep, while the upper electrode is a rod sharpened to a cone. The weight of powder loaded into the electrode is 50 mg. In order to fix the powder in the electrode crater, the powder is moistened with 3 drops of a 20% alcoholic solution of bakelite and the electrode then dried on an electric hot plate for 10-15 minutes. This precaution is essential in order to prevent the friable beryllium oxide powder from being thrown out of the crater during the initial stages of arc burning. The spectra are excited in a dc arc at a current strength of 12 amps, they are photographed in a ISP-22 spectrograph at a slit width of 10 μ. A two-stage attenuator with a relative transmission of 1 : 10 is fitted in front of the slit. Exposure time is 2 minutes; during this time complete combustion of the sample takes place. The photographic plates used are spectrographic type II.

The conditions used for determination of sodium are as follows: spectrograph ISP-51, slit width 10 μ, ac arc, current 5 amps, photographic plates panchrome. The lower electrode is a carbon rod with a crater 4 mm in diameter and 4 mm deep, while the upper electrode is a carbon rod sharpened to a cone. The subsequent procedure adopted for treatment of the results is the same as for determination of the remaining impurities.

Impurity lines and background are photometrically measured. In the short-wave part of the spectrum, the lines are measured photometrically in the strong stage of the spectrogram, while in the long wave part of the spectrum the lines are measured in the weak stage of the spectrogram. Calibration curves (Fig. 2) are constructed within the coordinates (log I, log C).* Conversion from blackening to intensity is carried out in a special calculating machine. For determination of the impurities in the concentrate, the result obtained by means of the calibration curve is divided by the enrichment coefficient; in this way the content of a given impurity in the original sample is obtained.

The analytical lines used and the sensitivity of the determination of the impurities are given in Table 1.

The accuracy and reproducibility of the method was checked by analyzing synthetic mixtures (25 mixtures, to each of which was added 20-25 elements), and also by comparing the results obtained during analysis of samples by the given method and by chemical methods (34 samples). The relative error, calculated as the mean arithmetic error of all of these determinations amounts to ± 20%. Nevertheless, near the sensitivity limit, particularly in the presence of a strong background, individual errors may be as high as 50-100%. This is particularly true for the determination of cadmium; this is a consequence of two factors: the low value of the slope for its calibration curve (Fig. 2), and the low contrast in the 2280 A region.

TABLE 2

Results of the Analysis of Synthetic Mixtures (Containing Impurities Whose Contents are Given in Terms of Beryllium Metal)

Element	Mixture 1, concentrate		Mixture 2, without enrichment	
	added	found	added	found
Mg	$5,3\cdot10^{-4}$	$5,5\cdot10^{-4}$	$1,5\cdot10^{-2}$	$1,4\cdot10^{-2}$
Ca	$2,3\cdot10^{-3}$	$2,6\cdot10^{-3}$	$4,5\cdot10^{-2}$	$6\cdot10^{-2}$
Ba	$6\cdot10^{-4}$	$5\cdot10^{-4}$	$9\cdot10^{-3}$	$1,1\cdot10^{-2}$
Al	$1,4\cdot10^{-3}$	$2,1\cdot10^{-3}$	$1,5\cdot10^{-2}$	$1,7\cdot10^{-2}$
Ti	$6\cdot10^{-4}$	$8,3\cdot10^{-4}$	$9\cdot10^{-2}$	$9,5\cdot10^{-2}$
V	$2\cdot10^{-4}$	$2,3\cdot10^{-4}$	$6\cdot10^{-2}$	$7,4\cdot10^{-2}$
Cr	$2\cdot10^{-4}$	$2\cdot10^{-4}$	$1,5\cdot10^{-2}$	$1,4\cdot10^{-2}$
Mo	$4\cdot10^{-4}$	$4\cdot10^{-4}$	$6\cdot10^{-2}$	$5,6\cdot10^{-2}$
Mn	$6,7\cdot10^{-5}$	$8,7\cdot10^{-5}$	$1,5\cdot10^{-2}$	$1,3\cdot10^{-2}$
Fe	$2,2\cdot10^{-3}$	$1,8\cdot10^{-3}$	$1,5\cdot10^{-2}$	$1,7\cdot10^{-2}$
Co	$4\cdot10^{-4}$	$4,3\cdot10^{-4}$	$3\cdot10^{-2}$	$3\cdot10^{-2}$
Ni	$4\cdot10^{-4}$	$5\cdot10^{-4}$	$4,5\cdot10^{-2}$	$4,4\cdot10^{-2}$
Cu	$9\cdot10^{-5}$	$8\cdot10^{-5}$	$1,5\cdot10^{-2}$	$1,7\cdot10^{-2}$
Ag	$6\cdot10^{-5}$	$8\cdot10^{-5}$	$1,5\cdot10^{-2}$	$1,4\cdot10^{-2}$
Zn	$2\cdot10^{-3}$	$5\cdot10^{-3}$	$9\cdot10^{-2}$	$6,8\cdot10^{-2}$
Cd	$2\cdot10^{-5}$	$1\cdot10^{-5}$	$9\cdot10^{-4}$	$6\cdot10^{-4}$
In	$2\cdot10^{-4}$	$2,8\cdot10^{-4}$	$2,6\cdot10^{-2}$	$4,8\cdot10^{-2}$
Sn	$4\cdot10^{-4}$	$5\cdot10^{-4}$	$6\cdot10^{-2}$	$5,7\cdot10^{-2}$
Pb	$4\cdot10^{-4}$	$5,2\cdot10^{-4}$	$4,5\cdot10^{-2}$	$4\cdot10^{-2}$
Sb	$6\cdot10^{-4}$	$6,3\cdot10^{-4}$	$4\cdot10^{-2}$	$4,2\cdot10^{-2}$
Bi	$2\cdot10^{-4}$	$2\cdot10^{-4}$	$2\cdot10^{-2}$	$1,8\cdot10^{-2}$
Ga	$2\cdot10^{-4}$	$3\cdot10^{-4}$	$6\cdot10^{-3}$	$5,9\cdot10^{-3}$
Tl	$2\cdot10^{-4}$	$2,5\cdot10^{-4}$	$2\cdot10^{-2}$	$1,8\cdot10^{-2}$
Te	$2\cdot10^{-4}$	$1,9\cdot10^{-4}$	$2\cdot10^{-2}$	$1,9\cdot10^{-2}$

Table 2 contains, as examples, the results of analysis of synthetic mixtures with and without the use of concentration.

SUMMARY

A chemicospectrographic method has been developed for the determination of 24 elements present as impurities in beryllium and its oxide. In order to concentrate the impurities (20-25 times) beryllium is separated in the form of its basic acetate by extraction with chloroform. The sensitivity of the determination of the ele-

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* In those cases where the blackening of the line of the element being determined is located on the straight-line part of the characteristic curve of the photographic plate (0.60 ≤ ΔS ≤ 1.80), the calibration curve is constructed with the coordinates (ΔS, log C), where ΔS is the difference between the blackening of the line and the background.

ments is increased to $10^{-4} - 10^{-5}\%$. The method can be used for the analytical control of the production of high-quality materials.

A method has been developed for the spectrographic analysis of samples without preliminary concentration of the impurities; this method, which can be used for controlling the production of commercial products, has a sensitivity of $10^{-3} - 10^{-4}\%$.

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A SEMI MICRO METHOD FOR THE ISOTOPIC ANALYSIS OF MATERIALS WITH A DEUTERIUM CONTENT APPROXIMATING TO 100%

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Modern physical methods of research make it possible to analyze compounds with high deuterium contents with reasonable accuracy (see [1], p. 5). Nevertheless, in those cases where these methods are for some reason difficult to carry out, the method described below, which does not require complicated apparatus can be used for isotopic analysis.

The test material (organic compound, ammonia) is burnt on cupric oxide under conditions which exclude ingress of atmospheric moisture, since the heavy water formed is very hygroscopic. The water formed, amounting to 0.2-0.3 ml is collected in a receiver containing calcium metal (for taking up the carbon dioxide and nitrogen oxides), and is distilled into a drawn-out test tube containing a quartz float which is used for measuring the density of the water.* Experimental accuracy is 0.05%.

1. Combustion of the Deuterium Compound

a. Combustion apparatus (Fig. 1). The material is burnt in tube 3 which is heated up to 700° by means of an electric oven. The reservoir 1 containing test material is sealed with an accurately fitting ground-glass cap. When ammonia is analyzed detail 10 is used instead of the cap, detail 10 is fitted by means of Wood alloy into a screw and is connected through a valve [2] with an ampoule containing the ammonia (Fig. 1, A). A receiver 5** is connected via a ground joint to the combustion tube. The system can be connected to the atmosphere or to a vacuum pump via an opening in joint 6. The apparatus ends up in tube 9 — in which the measurements are made — fitted with tap 7 connected to the receiver via a ground joint. 2, 4, and 8 are porous filters, filter 4 being fused in position after filling the tube with CuO. All the apparatus is made from quartz.

b. Preparation of the tube for combustion. Before each combustion, a stream of dry oxygen is passed through the heated tube for 20-30 minutes in order to oxidize any copper which has been formed by reduction during the previous combustion. The tube is then pumped out for a further 30-40 minutes in order to remove adsorbed moisture.

c. Combustion of organic material. A calibrated float is placed in tube 9, while a small lump (about 0.01 g) of pure calcium metal is placed in receiver 5. All joints and taps are smeared with vacuum grease and the apparatus is assembled. The test material is placed in reservoir 1. The ground joint of reservoir 1 is smeared with silicon grease and is then sealed with the cap. The system is connected to the vacuum pump via the opening in joint 6, and is exhaustively pumped out, using a vacustat for following the evacuation process. Taps 6 and 7 are closed and receiver 5 is cooled with liquid air, then by carefully heating reservoir 1 evaporation of the test material is commenced.

Whe evaporation is complete, the system is again evacuated for a short time. The Dewar vessel containing liquid air is removed, and the ice in the receiver allowed to melt; the water is then collected in the of receiver 5. When this is done the oxides react with the calcium metal. Tap 7 is next opened, and by cooling tube 9 with liquid air the water is driven into it. Tap 7 is closed.

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*A micro float method has been developed by A. L. Shatenshtein and E. A. Yakovleva (see [1], p. 183).

** V. R. Kalinachenko's design [5].

d. Combustion of ammonia. During the combustion of ammonia, nitrogen is formed which does not condense and gives rise to a pressure in the tube. Accordingly, combustion is not carried out in a vacuum. The system is assembled and pumped out so as to get rid of moisture as before, but then dry air is passed into the system through the opening in joint 6 which is connected to tubes packed with P_2O_5; on the side tube on joint 6 a bubble counter is fitted by means of a rubber tube; only after this has been done is the valve, to which the ampoule containing the liquid ammonia (about 0.4 ml) is connected, opened and combustion commenced. When the stream of bubbles cease the system is evacuated; all subsequent operations are the same as those described above.

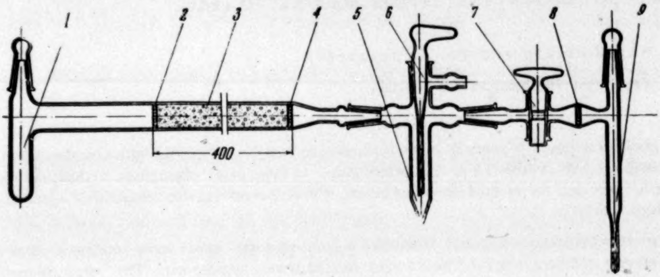

Fig. 1.

In order to ensure complete oxidation of ammonia it is necessary to carry out combustion slowly (2-2.5 hours).

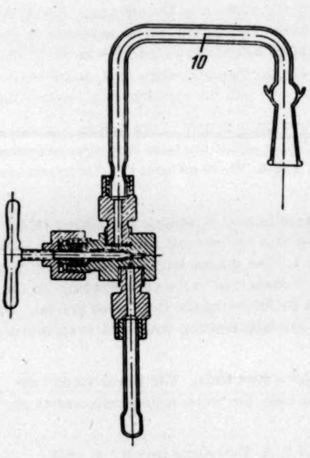

Fig. 2.

2. Isotopic Analysis of Water

The isotopic analysis of water reduces to the determination of the equilibrium flotation temperature of a micro-float, for which the equilibrium flotation temperature has been determined beforehand in heavy water with a known deuterium content similar to value to that expected for the test material. The deuterium concentration of the heavy water used for calibrating the float is established pycnometrically (see [1], p. 154).

A thermostat in which the temperature could be read and kept constant to an accuracy of ± 0.05° was used for the measurements. The temperature can be altered over a 10° range, which means that one float can be used for analyzing samples with deuterium concentrations differing within the limits of 2%.

In order to analyze preparations containing from 90 to 100% deuterium we used four floats calibrated by means of heavy water with deuterium concentrations (C_1) of 99.58, 97.89, 85.93, and 94.06%.

If the change in density of the quartz float (1.8 γ/ml per 1°) can be regarded as negligible, then the density of the water ($d_{4\,st.}^{t_1}$) used for calibration at the equilibrium flotation temperature of the float in it (t_1) can be assumed to be equal to the density of the test water ($d_{4\,\text{test}}^{t_2}$) at the equilibrium flotation temperature of the float in the latter (t_2).

In order to determine the deuterium concentration of the test material (C_2) on the basis of these results, it is necessary to know the density t_1 of the water taken as a standard. Its density is usually determined at 25°. Tables in which data is given on the density of deuterium oxide at various temperatures (see [1]) can be used for conversion to other temperatures if it is assumed that the density of heavy water with deuterium concentrations approximating to 100% change in the same way with temperature. When the deuterium concentration of the water used for calibration is 95%, and t_1 differs by 5° from 25°, such an assumption leads to an error in the determination of the density of the order of 0.00001, or to about 0.01 atom.% D in the determination of the concentration. Knowing the density of the test water at temperature t_2, it is possible, in a similar way to find its density at 25°, and, by dividing by the density of normal water at the same temperature (d_4^{25} = 0.997075 g/ml) to convert to $d_{25}^{25} = d_4^t / d_{4H_2O}$. From tables (see [1], appendix) it is then possible to find the deuterium concentration in the test water, and consequently, the deuterium concentration of the test material.

We shall illustrate the method of calculation, and the reproducibility of the results obtained by taking the analysis of deuteronaphthalene as an example.

$$t_1 = 21{,}7°; \quad d_{4\,(\text{st})}^{25} = 1{,}10011; \quad C_1 = 95{,}93\,\text{at.}\ \%.$$

We determine

$$d_{4\,(\text{st})}^{21,7°} = d_{4\,(\text{st})}^{25} + [d_{4\,(D_2O)}^{21,7} - d_{4\,(D_2O)}^{25}] =$$

$$= 1{,}10011 + (1{,}10509 - 1{,}10446) = 1{,}10074.$$

$$t_2 = 27{,}2°; \quad d_{4(\text{test})}^{27,2} = d_{4\,(\text{st.})}^{21,7} = 1{,}10074.$$

We determine

$$d_{4(\text{test})}^{25} = d_{4(\text{test})}^{27,2} + [d_{4\,(D_2O)}^{25} - d_{4\,(D_2O)}^{27,2}] =$$

$$= 1{,}10074 + (1{,}10446 - 1{,}10396) = 1{,}10124.$$

$$d_{25(\text{test})}^{25} = \frac{d_{4(\text{test})}^{25}}{d_{4\,(H_2O)}^{25}} = \frac{1{,}10124}{0{,}99707} = 1{,}10447.$$

Using tables (see [1] p. 226) we find for ΔS_{25}^{25} = 0.10449

$$C_2 = 96.99 \text{ atom.\%}$$

In a parallel analysis

$$t_2 = 27.1°, \ C_2' = 96.97 \text{ atom.\%}$$

Control experiments in which 0.3 ml of heavy water of known isotopic composition was passed through the setup under our analytical conditions, showed that the equilibrium flotation temperature of the float changes by 0.1°, which corresponds to a change in deuterium concentration of ± 0.02 atom.%. During actual analysis the equilibrium flotation temperature was reproduced with the same accuracy. The error indicated above which is introduced during calculation lies within the limits of ± 0.01 atom.%. Accordingly, the method described permits determinations to be carried out with an accuracy of 0.05 atom%.

We used this method for establishing the conditions which affect the isotopic purity of deuteroammonia obtained from magnesium nitride and heavy water containing 99.6% D_2O [3, 4]. It was found that when the deuteroammonia was prepared without observing any special precautions, its deuterium content did not exceed 95%. This low value for the deuterium concentration is a consequence of the fact that magnesium nitride reacts very readily with atmospheric moisture to form $Mg(OH)_2$ and NH_3. The NH_3 is adsorbed by the nitride. $Mg(OH)_2$, as shown experimentally, is capable under the conditions used for preparing ND_3 of exchanging with hydrogen, as a result of which the deuterium concentration drops.

When, however, the operation with magnesium nitride is carried out in a dry chamber, and, furthermore, when the nitride immersed in the cylinder used for preparing the ammonia, and evacuated beforehand on heating, is treated with small amount (1-2 ml) of liquid ND_3 which is used for desorbing the volatile ammonia from the surface of the Mg_3N_2 and the vessel, the latter having been pumped out before breaking the ampoule with the heavy water, then ammonia containing 98.6% D can be prepared.

SUMMARY

A semi micro method for the isotopic analysis of materials containing about 100% of deuterium is described. For the determination 0.2-0.3 ml of water from the combustion of the test material is required. The method is based on measurement of the density of the water by means of a micro float. The accuracy of the method is 0.05 atom.%.

The method is used for the analysis of organic compounds containing about 100% deuterium, and deuteroammonia obtained by the interaction of D_2O and Mg_3N_2.

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DETERMINATION OF MICRO AMOUNTS OF XENON BY MEANS OF THE MASS SPECTROMETER

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In carrying out the xenon method for the determination of the absolute age of minerals in actual practice [1], the basic problem is the isolation and measurement of micro amounts of xenon. Hitherto no method has been developed for the determination of small amounts ($10^{-6} - 10^{-5}$ cm^3) on this element. In this connection therefore we studied the possibility of using the MS-2M mass spectrometer for determination of xenon [2].

In order to calibrate the mass spectrometer, standards were prepared — mixtures of argon and xenon of known composition — in a high-vacuum setup schematically shown in Fig. 1. Traces of air were absorbed by keeping the argon and xenon over metallic calcium, first at 650° and subsequently at 300°. The amount of argon was measured in manometer 1. The same manometer served for the transfer of gases from one part of the setup to the other. Xenon was measured on the more sensitive manometer 2. Subsequent checks showed that the amount of argon present in the xenon used was about 1%.

Four pairs of standard mixtures were prepared: 1) 0.94% Xe and 0.095% Xe, 2) 0.29% Xe and 0.13% Xe, 3) 0.94% Xe and 0.26% Xe, 4) 1.18% Xe and 0.18% Xe. Results obtained with various standards coincided within the experimental error.

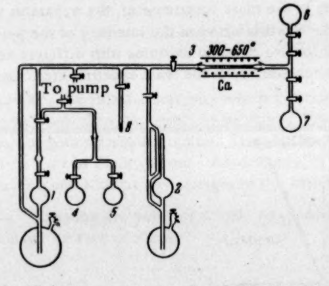

Fig. 1. High-vacuum setup: 1 and 2) McLeod gauges; 3) metallic calcium; 4 and 5) vessels for standards and control mixtures; 6) vessel containing argon; 7) vessel containing xenon; 8) activated carbon.

Using the mass spectrometer, determinations were carried out of the xenon content of control mixtures of varying composition prepared beforehand (Table 1).

The control mixtures were prepared in the same setup as the standards.

During the separation of xenon from minerals, one of the operations is the adsorption of the gases by means of cooled activated charcoal and subsequent desorption of the gases [1]. Accordingly, the control mixtures were also adsorbed with activated charcoal at -183° before carrying out measurements on the mass spectrometer.

In the course of the work it was established that during desorption from the activated charcoal of the mixture of argon and xenon, there occurs partial separation of these gases. Xenon is held very firmly by the charcoal, so that some of it still remains adsorbed even at a temperature of 320°.

In an experiment where 10 g of activated charcoal was used, about 30% of the amount of xenon taken remained adsorbed. When using 0.1 g of charcoal at a temperature 320°, 10-12% of the xenon was not desorbed.

Only by decreasing the weight of the adsorbent to 0.04 g was it found possible to desorb all the xenon completely.

Moreover, it was observed that partial adsorption of the xenon occurs in the traps cooled with liquid air. 20-30% of the amount of xenon could be held on the trap walls, accordingly, before admitting the samples into the mass spectrometer; a trap containing a mixture of alcohol and dry ice (temperature −78.5°) was used for freezing the vapors.

TABLE 1

Xe taken, $cm^3 \cdot 10^{-5}$	Xe found, $cm^3 \cdot 10^{-5}$			Deviation of the mean value found from that actually taken, %	Xe taken, $cm^3 \cdot 10^{-5}$	Xe found, $cm^3 \cdot 10^{-5}$			Deviation of the mean value found from that actually taken, %
	pressure method	method of relative sensitivities	by the two methods			pressure method	method of relative sensitivities	by the two methods	
0,342	0,314	0,328	0,321	− 6	1,82	2,06	1,97	2,03	+12
0,470	0,446	0,470	0,458	− 3	1,90	1,47	1,50	1,49	−21
0,505	0,616	0,500	0,558	+12	1,90	2,00	2,05	2,02	+ 6
0,531	0,504	0,531	0,517	− 3	2,29	2,43	2,50	2,46	+ 7
0,609	0,469	0,609	0,539	−12	2,36	2,18	2,60	2,39	+ 1
0,905	0,886	0,751	0,816	−10	2,67	2,78	2,78	2,78	+ 4
0,914	1,28	0,940	1,11	+10	3,28	2,85	2,79	2,82	−14
1,51	1,72	1,42	1,57	+ 3	4,54	4,84	4,54	4,69	+ 3
1,57	1,53	1,51	1,52	− 3	4,85	4,85	4,75	4,80	− 1
1,62	1,78	1,52	1,65	+ 2					

A tube containing heated calcium metal was fitted into the admittance system of the mass spectrometer, so that any possible small ingress of air could not affect the results.

Two methods of measurement on the mass spectrometer were used: the pressure method and the method of relative sensitivities.

The Pressure Method

After establishing a pressure of $1 \times 10^{-7} - 2 \times 10^{-7}$ mm Hg in the mass spectrometer, the apparatus was adjusted to the xenon isotope with a mass of 132. The form of the relation between the intensity of the peak and the pressure in the region of the ionic source was determined for two standard mixtures with different xenon contents. The pressure p was measured on the standard ionization manometer of the mass spectrometer. Curves

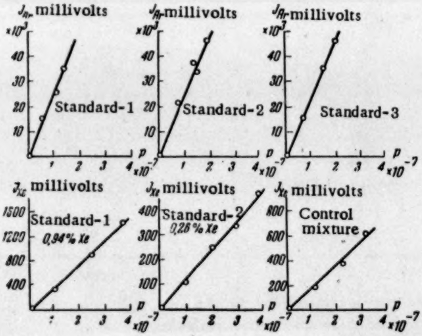

Fig. 2. Calibration curves.

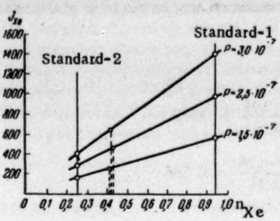

Fig. 3. Determination of xenon in mixtures: n^x_{Xe} = 0.4, 0.42, 0.41; average 0.42 $V^x_{Xe} = \frac{0.42\cdot 4.84\cdot10^{-3}}{100} =$ $2.04\cdot10^{-5}$ cm^3 Xe.

of $J_{Xe} = f(p)$ were constructed for both standards, where J_{Xe} is the intensity of the peak in mv, p is the pressure in the ionic source and n is the percentage content of the mixture. As a rule, the peak intensity was proportional to the pressure in the region of the ionic source. Only for $p > 5 \times 10^{-7}$ mm Hg did the linear relation break down. As an illustration we have given curves (Fig. 2. and 3) which were obtained in one of the experiments (4.84×10^{-3} cm^3 Ar and 1.90×10^{-5} cm^3 Xe).

From the results obtained, calibration curves $n^x_{Xe} = f(J_{Xe})_p$ = const. were constructed for several pressures.

The values of the peak intensity Xe^{132} were then measured for the test mixtures at various pressures p. Curves $J_{Xe} = f(p)_x$ were constructed. Using these results and the calibration straight lines, it is possible to find the mean value n^x_{Xe} the percentage content of xenon in the test mixture (Fig. 3).

Construction of the curves is not obligatory nevertheless we thought it was more convenient to adopt a graphical method of calculation, since any deviation from the proportional relationship will not escape observation in this case.

The Relative Sensitivity Method

The sensitivity of the mass spectrometer to argon and xenon is determined by means of the standard mixtures:

$$\Delta J_{Ar}/\Delta P_1 = S_{Ar} \quad \Delta J_{Xe}/\Delta P_2 = S_{Xe}\cdot n_{Xe}/n_{Ar}.$$

Here, $\Delta J_{Ar}/\Delta P_1$ and $\Delta J_{Xe}/\Delta P_2$ are the changes in intensity on changing the pressure in the ionic source by 1×10^{-7} mm Hg, where $\Delta J_{Xe} = \Delta J^{132}_{Xe}/N$, N being the fraction of the Xe^{132} isotope in the mixture of xenon isotopes; S is the sensitivity; n_{Xe} and n_{Ar} are the percentage contents in the standard mixtures. From these it is easy to find the relative intensity:

$$\frac{\Delta J_{Ar}\cdot\Delta P_2}{\Delta P_1\cdot\Delta J_{Xe}} = \frac{S_{Ar}}{S_{Xe}}\cdot\frac{n_{Ar}}{n_{Xe}}, \quad K = \frac{S_{Ar}}{S_{Xe}} = \frac{\Delta J_{Ar}\cdot\Delta P_2\cdot n_{Xe}}{\Delta J_{Xe}\cdot\Delta P_1\cdot n_{Ar}}.$$

Here K is the relative intensity which indicates how many times the sensitivity of the mass spectrometer towards argon is less than its sensitivity to xenon. The value of K was determined separately in each experiment on the basis of both standard mixtures. Usually, the relative sensitivity was about 0.5 and changed somewhat with the adjustment of the apparatus. Accordingly, it was found essential to carry out the measurements as rapidly as possible and without any changes in the adjustment (tuning) of the mass spectrometer.

Knowing the value of K and $\Delta J_{Ar}\cdot\Delta P_2/\Delta J_{Xe}\cdot\Delta P_1$ for the test mixture, it is possible to find its percentage content of xenon:

$$\frac{n_{Ar}}{n_{Xe}} = \frac{1}{K}\cdot\frac{\Delta P_2\cdot\Delta J_{Ar}}{\Delta P_1\cdot\Delta J_{Xe}}; \quad \frac{100-n_{Xe}}{n_{Xe}} = \frac{1}{K}\cdot\frac{\Delta P_2\cdot\Delta J_{Ar}}{\Delta P_1\cdot\Delta J_{Xe}}.$$

$$\text{From which } n_{Xe} = 100/\left(\frac{1}{K}\cdot\frac{\Delta P_2\cdot\Delta J_{Ar}}{\Delta P_1\cdot\Delta J_{Xe}}+1\right).$$

In practice the experimental determination of the values of $\Delta J_{Ar}/\Delta P_1$ and $\Delta J_{Xe}/\Delta P_2$ for the control and standard mixtures permitted calculations to be made according to both methods.

As an example we have given below the calculation of the xenon content on the basis of the experimental results given above (Figs. 2 and 3).

The value of K is determined:

$$\text{from standard} \quad -1: K = \frac{47\,000 \cdot 4 \cdot 10^{-7} \cdot 0{,}94}{2 \cdot 10^{-7} 1600 \cdot 99{,}06} = 0{,}555$$

$$\text{from standard} \quad -2: K = \frac{50\,000 \cdot 3 \cdot 10^{-7} \cdot 0{,}26}{2 \cdot 10^{-7} \cdot 335 \cdot 99{,}74} = 0{,}585$$

The mean value of K = 0.570 ± 0.015.

Next, we find n^x_{Xe}:

$$n^x_{\mathrm{Xe}} = 100\left(\frac{1 \cdot 48\,000 \cdot 3 \cdot 10^{-7}}{0{,}57 \cdot 2 \cdot 10^{-7} \cdot 530} + 1\right) = \frac{100}{242} = 0{,}41\ \%.$$

Converting to amounts by volume, we get:

$$\frac{4{,}84 \cdot 10^{-3} \cdot 0{,}41}{100} = 1{,}88 \cdot 10^{-5}\ \mathrm{cm}^3.$$

All the results obtained are given in Table 1. The deviation of the mean amount of xenon actually found from that taken amounts to ± 8%. The accuracy of both methods of measurement proved to be approximately the same.

An additional check on the reliability of the results obtained was a determination of the xenon content of uraninite from Chernaya Salma which we carried out. The xenon content of this sample had been determined earlier by the usual volumetric method ([1]. The results obtained by both methods were found to be in good agreement with each other; this testifies to the reliability of the method suggested above for the determination of micro amounts of xenon (Table 2).

TABLE 2

Method	Sample wt., g	Amounts of xenon per gram of mineral, cm^3
Mass spectrometric	11.4	$(0.75 \pm 0.12)\ 10^{-6}$
Volumetric	350	$(0.77 \pm 0.06)\ 10^{-6}$

It follows from this work that:

During the quantitative determination of xenon, measures should be taken to prevent loss of xenon as the result of adsorption.

Using a mass spectrometer, it is possible to determine $1 \times 10^{-6} - 5 \times 10^{-5}\ \mathrm{cm}^3$ of xenon with a mean accuracy of ± 8%.

The accuracy of the pressure method and the method of relative sensitivity is approximately the same.

SUMMARY

Reference and control mixtures of argon and xenon with a definite content of xenon have been prepared by means of a vacuum apparatus. A MS-2M mass spectrometer has been used for determining about $10^{-5} - 10^{-6}\ \mathrm{cm}^3$ of xenon in the control mixtures.

Two methods have been used: the pressure method and the method of relative sensitivity. A mixture of solid CO_2 and ethanol ($-78.5°$) was used instead of liquid oxygen in the vacuum traps, so as to prevent loss of xenon resulting from absorption. Loss of xenon on account of the difficulty of desorbing it from the activated charcoal was overcome by using small amounts of adsorbent (0.04 g). The mean experimental accuracy for the determination of $10^{-5} - 10^{-6}$ cm^3 of xenon is ± 8%. The radiogenic xenon content of Black Salma uraninite has also been determined. The value obtained by the mass-spectrometric method (0.75×10^{-6} cm^3/g) was found to be in good agreement with that obtained by a volumetric method (0.77×10^{-6} cm^3/g).

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CONDUCTOMETRIC ANALYSIS OF NATURAL WATERS, COMMUNICATION 2. DETERMINATION OF MAGNESIUM AND ANIONS[*]

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Determination of Magnesium

In recent years a large amount of work has been published on the use of Complexon III for analytical purposes. Among the papers which have appeared are ones devoted to the complexonometric determination of magnesium in water [1-2]. Nevertheless, the complexonometric method of determining magnesium in colored and turbid water is difficult, and is often impossible because of the difficulty of establishing the color change of the indicator. Moreover, iron, when present in the test water in amounts greater than 10 mg/liter, also interferes. Calcium, just like magnesium, forms with Complexon III at pH 10, a stable compound, readily soluble in water, so that calcium, too, interferes with magnesium determination. Mannite [3] or ammonium oxalate [1] has been recommended for preventing interference by calcium. In the method which we have developed calcium was precipitated with oxalate[**]; the suspension obtained was titrated with a solution of Complexon III. Belcher and Wilson [4] indicate that magnesium hardness can be determined after precipitation of the calcium with a soluble oxalate. Titration can be carried out in the presence of the precipitated calcium oxalate.

The suggested method was worked out using synthetic mixtures made up from standard solutions of 0.1 N calcium chloride and 0.1 N magnesium sulfate; the applicability of the method in the presence of large amounts of aluminum and iron was established.

It was found that aluminum and iron, given in large amounts (100 mg/liter), do not interfere. On addition of sodium oxalate to test solutions containing aluminum and iron, there are formed oxalate compounds which are soluble in water, and which are broken down on addition of an ammoniacal buffer solution (pH 10), since they are unstable in an alkaline medium; under these conditions therefore the hydroxides of these metals are formed, and they do not interfere with the process of conductometric titration.

Apparatus. A vessel fitted with a cylindrical piston stirrer was used for conductometric titration [6]. The reagent was added by means of a pneumatic microburet [7]. Titration was carried out on an apparatus of the Toropov system [8].

The 0.1 N solution of Complexon III was standarized by means of a standard mixture of 0.01 N solutions of calcium chloride[***] and magnesium sulfate[****] taken in the ratio of 3 : 1 by volume, and prepared by mixing the 0.1 N solutions.

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[*] For Communication 1, see Bull. Acad. Sci. Tadzh. SSR.

[**] Sodium oxalate was chosen as the reagent, since sodium ions have a lower mobility than potassium and ammonium ions.

[***] 5.005 g of calcium carbonate (chemically pure grade dried at 110° for 1 hour and cooled in a desiccator over calcined calcium chloride) was dissolved in the minimum amount of concentrated hydrochloric acid contained in a liter standard flask. Whe solution was complete the volume of the contents of the flask was made up to the mark with distilled water and thoroughly mixed.

[****] 12.325 g of chemically pure grade magnesium sulfate containing seven molecules of water was dissolved in water in a liter standard flask and the volume made up to the mark with distilled water; the whole was then thoroughly mixed. The concentration of the solution thus obtained was checked [5], and, when necessary, a correction applied for the normality.

25 ml of the standard mixture (calcium : magnesium = 3 : 1) was pipetted into a 50 ml beaker, and 1 drop of Methyl Red and 0.1 N hydrochloric acid added to the appearance of a rose color. The solution was boiled on an electric hot plate and evaporated to a volume of 5-10 ml; the solution was then cooled to 80° and 1 drop of a saturated solution of sodium oxalate added to it, followed by dropwise addition, with stirring, of 0.5 ml of an ammoniacal buffer mixture with a pH of 10 (0.1 N NH_4OH and 0.1 N NH_4Cl mixed in the proportion of 1 : 5). After cooling to room temperature the solution was quantitatively transferred to the titration vessel, and its volume made up to 50 ml; it was finally conductometrically titrated with Complexon III. From the amount of Complexon III used up in the titration the number of mg of magnesium corresponding to 1 ml of titrant was calculated.

For determination of the magnesium content of natural water, 5-25 ml of the test water, depending on the expected magnesium content, was measured into a 50 ml beaker. One drop of Methyl Red was added to the solution; this was followed by addition of 0.1 N hydrochloric acid until the color of the indicator had turned to rose. The solution was heated on an electric hot plate (when the color of the indicator changed to yellow some more 0.1 N hydrochloric acid was added to change the color back to rose* again) and the procedure outlined above then followed.

From the amount of 0.1 N Complexon III solution used up, the magnesium content of the test sample was then calculated.

The applicability of the method was checked on natural waters, the magnesium content of which was determined by the method suggested, and by the pyrophosphate method [9], using the filtrate obtained after removal of calcium by the oxalate method. The results obtained, which are given in Table 1, show that the suggested method can be used for the determination of magnesium in natural waters.

TABLE 1

Determination of Magnesium in Natural Waters

Ca^{2+} content of the water, mg/liter	Conductometric determination		Gravimetric determination	
	water taken, ml	Mg^{2+} found, mg/liter	water taken, ml	Mg^{2+} found, mg/liter
28,27	25	16,95	1000	16,98
43,61	25	19,44	1000	19,42
56,54	10	33,61	1000	33,91
83,92	10	43,21	1000	43,78
76,09	10	48,62	1000	48,99
95,64	10	62,42	1000	62,90
141,10	5	72,02	1000	72,70

Determination of Anions

Usually, during the analysis of natural waters, sulfate, chloride, and bicarbonate are determined. In this connection, therefore, a method has been developed for the conductometric analysis of natural waters for these anions on the basis of a technique described earlier [6-8, 10].

Determination of Sulfates. Test water containing 2-10 mg of sulfate was measured into the titration vessel. 1-2 drops of Methyl Red was added to the solution followed by 0.1 N hydrochloric acid to give a neutral reaction. Dry, ground-up barium sulfate (about 100 mg) was then added, followed by 0.5 ml of a saturated solution of Methyl Violet. The solution was then mixed and 0.5 ml of a standard solution of 0.1 N barium chloride (12.21 g $BaCl_2 \cdot 2H_2O$ in 100 ml water) measured out with a micropipet added; the volume was finally made up to 100 ml with water. The solution was thoroughly mixed and excess barium chloride titrated conductometrically with 1 N sodium sulfate solution (standardized conductometrically against $BaCl_2$).

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*Excess acid must be avoided.

Determination of chlorides. Test water containing 2-20 mg of chloride was measured out into the titration vessel. One drop of Methyl Red was added, followed by 1 N nitric acid until the solution was neutral, 2-3 drops of nitric acid in excess was then added. The solution was mixed and water added to bring the volume up to 25 ml, the solution was conductometrically titrated with 0.5 N mercuric nitrate (8.340 g of mercuric nitrate was dissolved in water contained in a 100 ml standard flask and conductometrically standardized against 0.1 N potassium chloride). When, on addition of reagent there was observed the appearance of a yellow turbidity, the test had to be prepared again by adding to it, after neutralization, 6-7 drops of nitric acid.

Determination of carbonate hardness. a) Determination of carbonate hardness in the absence of phosphates. Test water containing 0.2-0.02 mg. equivalents of carbonate was measured into the titration vessel. 100 mg of dry barium chloride was added, followed by 5 ml of 0.01 N hydrochloric acid and 5 ml of 0.01 N acetic acid. When iron was present, sodium fluoride was added until the solution was decolorized, or the acetic acid was substituted by 50 mg of citric acid. The volume of the mixture was adjusted to 50 ml with distilled water and the solution conductometrically titrated with 0.1 N $Ba(OH)_2$ (standardized conductometrically with 0.01 N HCl).

b) Determination of carbonate hardness in the presence of phosphates. For removal of phosphates the test water was measured into a 50 ml beaker and 5 ml of 1% barium chloride solution added. After 2-3 minutes, when the precipitate had settled out, the solution was filtered through a filter of the minimum possible size into the titration vessel. The beaker in which precipitation had been carried out was rinsed three times with 1 ml lots of cold water which was then poured through the same filter each time. Finally the precipitate on the filter was washed with pure distilled water and the filtrate obtained titrated as described above.

Determination of total hardness. Test water containing 0.06-0.03 mg · equivalents of calcium and magnesium was measured into a 50 ml flask. One drop of Methyl Red was added, followed by hydrochloric acid until the color of the solution was red. The solution obtained was boiled on an electric hot plate for several minutes. When the color of the solution changed during the boiling process, some more hydrochloric acid was added.

The solution was cooled to room temperature under tap water, and quantitatively transferred to the titration vessel; distilled water was added to bring the volume up to 50 ml and 0.5 ml of a buffer solution with pH 10* added. The solution prepared in this way was mixed and titrated conductometrically with 0.1 N Complexon III solution.

TABLE 2

Analysis of Natural Waters for Anions and Hardness by Classical and Conductometric Methods

Method	SO_4^{2-}, mg/liter	Cl^-, mg/liter	Carbonate hardness, mg · · equivalents	Total hardness, mg · equivalents
Conductometric	56,40	20,39	3,01	3,85
Classical	57,5	20,2	2,95	3,86
Conductometric	239,96	107,64	6,22	9,99
Classical	240,4	107,74	6,20	10,00
Conductometric	399,3	266,2	2,20	7,79
Classical	400,5	266,0	2,18	7,76
Conductometric	599,90	84,78	10,83	17,3
Classical	601,5	84,3	10,8	17,28

The method suggested has been checked on natural waters; analysis was carried out by generally accepted methods and by the suggested methods. The results obtained are given in Table 2.

It is clear from these results that the method suggested can be used for mass analyses of water.

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*The buffer solution was added last in order to avoid precipitation of magnesium hydroxide from water containing large amounts of magnesium.

SUMMARY

A rapid conductometric method has been developed for the determination of magnesium, anions, and hardness in natural, turbid, and colored waters.

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**Russian translation.

ELEMENTAL ORGANIC ANALYSIS BY THE "WET COMBUSTION METHOD"

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Analysis of organic compounds using the technique of complete oxidation by means of oxidizing agents in solution is called the wet combustion method. Kjeldahl determination of nitrogen is of this type. Similar methods have been known for a long time and are often used for decomposing organic materials with the aim of determining one element. Such methods are only rarely used for the simultaneous determination of several elements. The first to indicate such a possibility during the analysis of organometallic compounds was Messinger in 1888 [1].

The oxidizing agent used most frequently is chromic acid or its salts mixed with concentrated sulfuric acid or mixed with sulfuric and phosphoric acids. Houghton [2] and Van Slyke [3] have given literature reviews.

As a rule, it is necessary to carry out "complete combustion"; for this purpose, the gaseous reaction products are usually passed through a heated tube containing cupric oxide. Nevertheless, this method has a number of essential drawbacks. In particular, the greatest difficulties arise during the determination of halogen-containing materials [4].

In the technique we wish to propose the catalyst which we used for complete combsution was chromic oxide. This enabled us to avoid a number of difficulties.

Fedoseev and Pavlenko [5] used chromic oxide as a catalyst for surface combustion during elemental analysis. Klimova, Korshun, and Bereznitskaya [6] have used it during microelemental analysis of organosilicon compounds.

The combined combustion method which has been developed, and which can be called the chromic method, is of great interest, particularly for production laboratories. Obviously, direct determination of hydrogen, sulfur, and chromium is impossible, but, on the other hand, the method does permit simultaneous determination of many other elements, in addition to carbon and nitrogen, on one aliquot. Using this technique, it is possible to analyze not only dry materials, but also solutions of organic compounds in water or sulfuric acid. The simplicity of the apparatus, and the possibility of working with aliquots over a wide range, makes the method very attractive.

Determination of carbon. The oxidation mixture which we use consists of concentrated sulfuric acid and a concentrated aqueous solution of chromic acid, which is gradually added in small portions during the oxidation process. For ensuring complete combustion, specially prepared chromic oxide deposited on lumps of pumice was used. Combustion of the aliquot of organic test materials is carried out in the apparatus shown in the diagram.

10 ml of concentrated sulfuric acid is placed in the reaction flask 3, while 1-2 ml of chromic acid is placed in the side tube of this vessel. A stream of oxygen is then passed through at the rate of about 50-60 ml/ /minute, and the tared tube 11 connected; by lifting the stopper a little beaker containing the test aliquot is then lowered into the reaction flask. The chromic acid is added from the side-tube dropwise, the reaction flask

being rotated carefully around joint 6 which is greased, like joints a and b, with phosphoric acid. The flask is immersed in a bath heated to 150-160°. The gaseous reaction products, which may contain some products of incomplete combustion (CO, CH_3COOH, etc.), together with the hydrogen stream pass into the heated tube (700-750°) containing chromic oxide, here combustion is completed; the final oxidation products then pass through flask 8 (the purpose of which is indicated below), through concentrated acid 9, and Anhydrone 10 for purifying and drying the CO_2 formed. Carbon is determined from the increase in weight of tube 11 which is filled with ascarite and Anhydrone. Tube 12 containing the same packing is connected to tube 11 (12 is not shown in the diagram). Combustion does not take longer than 30 minutes.

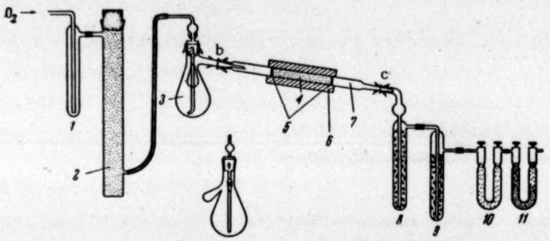

Fig. 1. Wet combustion apparatus: 1) Bubble counter filled with concentrated sulfuric acid; 2) ascarite column for drying the oxygen; 3) reaction flask; 4) catalyst, 80 mm long; 5) loose stopper of asbestos; 6) electric oven at 700-750°; 7) quartz tube 200 mm long and 10-12 mm in diameter; 8) vessel containing glass rods (a plug of glass wool is placed in the bulb) moistened with an acetic acid solution of hydrazine hydrate; 9) vessel containing glass rods moistened with concentrated sulfuric acid; 10) tube containing Anhydrone 11) tube containing ascarite and Anhydrone.

TABLE 1

Determination of Carbon

Test material	Sample wt., mg	CO_2, mg	C, %		Difference
			found	calc.	
Salicylic acid $C_7H_6O_3$	110,80	245,99	60,59		—0,28
	70,94	158,24	60,88	60,87	+0,01
Ethylanthraquinone $C_6H_{12}O_2$	60,81	181,54	81,48		+0,14
	59,84	178,63	81,47	81,34	+0,13
Acenaphtnene $C_{12}H_{10}$	54,43	186,97	93,75		+0,29
	54,22	186,03	93,63	93,46	+0,17
Cholesterol $C_{27}H_{46}O$	53,68	164,68	83,72		—0,15
	60,12	184,74	83,86	83,87	—0,01
Xanthone $C_{13}H_8O_2$	49,82	145,02	79,44		—0,14
	52,38	152,83	79,63	79,58	+0,05
Diethyl ester of dimethylbenzodifurane dicarboxylic	64,84	155,64	65,51	65,45	+0,06
acid $C_{18}H_{18}O_6$	60,59	145,68	65,62		+0,17

Simultaneous determination of carbon and other elements can be carried out in the same apparatus. Modifications to the technique are only necessary in the case of combustion of chlorine-containing materials.

Simultaneous determination of carbon and chlorine (or bromine). During the oxidation of chlorine-containing organic materials by the chromic method, formation of volatile chromyl chloride occurs; when the latter passes into the tube containing chromic oxide, it is decomposed to liberate chlorine, oxygen, and to form chromic oxide. Chromyl chloride is also partially decomposed by water vapor with formation of hydrogen chloride. The cupric oxide used earlier, forms, in this case, volatile chloride compounds. Bromine-containing organic materials are oxidized with formation of elemental bromine.

A solution of hydrazine hydrate neutralized with acetic acid to a pH of 6 is used for absorption of the halogens. Under these conditions the halogens are completely absorbed while the CO_2 is not absorbed.

The aliquots of halogen-containing materials are subjected to combustion in the same way as that described for the determination of carbon. During the analysis of chlorine-containing compounds, the amount of chromic acid taken is 1-2 ml more, and it is added gradually dropwise before starting to heat, addition being carried out as the red-brown fumes of chromyl chloride are driven out of the flask; about a third of the amount of chromic acid taken is left in the side tube. Flask 3 is then immersed in the heated bath so that the side tube of the flask touches the liquid in the bath. This ensures that the chromyl chloride deposited on the flask walls is decomposed by water vapor. The halogens are absorbed in vessel 8 containing glass rods moistened with the acetic acid solution of hydrazine hydrate (pH 6). The remaining operations are the same as those described for the determination of carbon. The chloride or bromide ions contained in vessel 8 are titrated by the Volhard method.

TABLE 2

Simultaneous Determination of Carbon and Chlorine (or Bromine)

Test material	C, in %		Difference	Hal, in %		Difference
	found	calc.		found	calc.	
p-Chlorobenzoic acid	53,50	53,70	—0,20	22,44	22,65	—0,21
$C_7H_5O_2Cl$	53,57		—0,13	22,54		—0,11
2,6-Dichloroquinone	40,61	40,72	—0,11	39,96	40,06	—0,10
$C_6H_2O_2Cl_2$	40,82		+0,10	40,10		+0,04
p-Nitrochlorobenzene	45,83	45,74	+0,09	22,44	22,50	—0,06
$C_6H_4O_2NCl$	45,62		—0,12	22,35		—0,15
4-Chloro-5-methyl-2-iso-	64,93	65,04	—0,11	19,35	19,20	+0,15
propylphenol $C_{10}H_{13}OCl$	65,12		+0,08	19,25		+0,05
Dinitrochlorobenzene.	35,38	35,58	—0,20	17,34	17,50	—0,16
$C_6H_3O_4N_2Cl$	35,67		+0,09	17,56		+0,06
2,3-Dibromo-4-naphtha-	38,24	38,01	+0,23	50,51	50,58	—0,07
quinone $C_{10}H_4O_2Br_2$	38,32		—0,31	50,31		—0,27
2-Bromo-1,4-naphtha-	52,74	52,62	—0,12	22,06	21,88	+0,18
quinoneacetoacetic ester $C_{16}H_{13}O_5Br$	52,69		+0,07	21,83		—0,05
Bromonitrobenzene	35,59	35,67	—0,08	39,40	39,56	—0,16
$C_6H_4O_2NBr$	35,79		+0,12	39,60		+0,04

Thus, the use of chromic oxide as a catalyst for ensuring complete combustion, together with the use of an acetic acid solution of hydrazine hydrate for absorption of the halogens, make it possible to carry out simultaneous determination of carbon and chlorine (or bromine).

During the analysis of materials for their contents of carbon, or of carbon and halogen, it is possible to carry out combustion of two or even three aliquots in the same flask. For this purpose, the reaction flask is not disconnected and the sulfuric acid is not changed, the only additional operation is the addition of more chromic acid and a further aliquot of test material.

Simultaneous determination of carbon, chlorine, and nitrogen. When the nitrogen-containing compound gives ammonia in concentrated sulfuric acid, then nitrogen can be determined in the material as well as carbon and chlorine. For this purpose the contents of the reaction vessel 3, after combustion, is transferred to a

Kjeldahl flask excess alkali is then added and the ammonia is distilled over in the usual apparatus into a standard acid solution. In this way it is possible to determine nitrogen in amines, nitriles, pyrrolidines, indoles, etc.

TABLE 3

Simultaneous Determination of Carbon, Chlorine, and Nitrogen

Test material	C, %		Difference	Cl, %		Difference	N, %		Difference
	found	calc.		found	calc.		found	calc.	
Ester of o-hydroxybenzoic acid and the hydrochloride of N-ethyl-α-methylpyrrolidine $C_{14}H_{20}O_3NCl$	58,61	58,85	−0,24	12,18	12,41	−0,23	4,90	4,90	0,0
	58,87		+0,02	12,25		−0,16	5,06		+0,16
The ester of cinnamic acid and the hydrochloride of N-ethyl-α-methylpyrrolidine $C_{16}H_{22}O_2NCl$	65,00	64,96	+0,04	11,87	11,98	−0,11	4,69	4,74	−0,05
	64,88		−0,08	11,82		−0,16	4,83		+0,09
The naphthyl ester of the hydrochloride of N-propyl-α-methylpyrrolidine $C_{18}H_{24}O_2NCl$	67,26	67,17	+0,09	11,25	11,02	+0,23	4,52	4,38	+0,17
	67,11		−0,06	11,20		+0,18	4,49		+0,14
Ethyl oxamate $C_4H_7O_3N$	41,30	41,02	+0,28				12,25	11,96	+0,29
	41,03		+0,01				11,99		+0,03
Dinitrylsuccinic acid $C_4H_2N_2$	61,46	61,53	−0,07				35,84	35,88	−0,04
	61,78		+0,25				36,01		+0,13
1-Phenyl-2-methyl-3-carbethoxy-5-acetoxyindole $C_{20}H_{19}O_4N$	71,42	71,20	+0,22				4,00	4,15	−0,15
	71,49		+0,29				4,25		+0,10

TABLE 4

Simultaneous Determination of Carbon and Nitrogen in Compounds Containing Two forms of Nitrogen ("oxidizing" and "reducing")

Test material	C, %		Difference	N*, %		Difference
	found	calc.		found	calc.	
3-Methyl-4-cyanoethylpyrazolone-5 $C_7H_9ON_3$	55,62	55,62	0,0	9,41	9,26	+0,15
	55,61		−0,01	9,44		+0,18
1-Cyanoethyl-3-isobutylpyrazolone-5 $C_{10}H_{15}ON$	62,42	62,15	+0,27	7,30	7,25	+0,05
	62,24		+0,09	7,22		−0,03
1-Phenyl-3-methyl-4-cyanoethylpyrazolone-5 $C_{13}H_{13}ON_3$	68,67	68,70	−0,03	6,30	6,16	+0,14
	68,78		+0,08	6,15		−0,01
The tricyanoethyl ester of trimethylol nitromethane $No_2 \cdot C(CH_2O \cdot CH_2CH_2CN)_3$	50,55	50,32	+0,23	13,65	13,54	+0,11
	50.49		+0,17	13,76		+0,22
m-Nitroaniline $C_6H_6O_2N_2$	52,22	52,17	+0,05	10,18	10,14	+0,06
	52,19		+0,02	10,08		−0,04

It is of interest to note that determination of nitrogen in such compounds can be carried out in the presence of other forms of nitrogen (−NO_2, −NH−NH−, etc.). Examples of such determinations are given in Table 4.

Accordingly, in a number of cases, the wet combustion method can be used for the separate determination of various forms of nitrogen.

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*Nitrogen content calculated for the groups −CN and −NH_2.

The method for the simultaneous determination of carbon, halogens, and nitrogen is also suitable for the analysis of compounds containing other elements. The combustion technique remains the same. When no halogens are present, flask 8 can be omitted.

Analysis of organic materials containing metals. During the oxidation of organic compounds containing metals, the latter, usually, remain in the reaction flask as the sulfates, since in this case complete mineralization occurs. The presence of chromic acid may lead to difficulties when metals are to be determined. Accordingly, when combustion is complete sexivalent chromium is reduced to the trivalent state by addition of a few drops of methanol. Complex compounds containing iron or copper were taken as test materials.

Iron was determined by treating the sulfuric acid solution with sodium sulfide, and, after removal of H_2S, the reduced iron was titrated with potassium dichromate in the presence of diphenylamine.

For the analysis of copper complexes, the copper was determined iodometrically in the sulfuric acid solution. This solution was then used subsequently for determination of nitrogen, the ammonia formed being distilled off in the usual way. Table 5 contains some examples of the analysis of complex compounds containing iron or copper.

TABLE 5

Simultaneous Determination of Carbon and Iron or of Carbon, Nitrogen, and Copper

Test material	C, %		Difference	N, %		Difference	Metal, %		Difference
	found	calc.		found	calc.		found	calc.	
Iron isovalerylacetonate	60,06	60,13	–0,07				11,45	11,65	–0,20
$C_{24}H_{39}O_6Fe$	60,00		–0,13				11,35		–0,30
Ferrocene $C_{10}H_{10}Fe$	64,77	64,56	+0,21				30,16	30,02	+0,14
	64,73		+0,17				29,93		–0,09
Diacetylferrocene	62,43	62,25	+0,18				20,56	20,68	–0,12
$C_{14}H_{14}O_2Fe$	62,42		+0,17				20,77		+0,09
Copper methylaminoacetylacetonate	50,14	50,06	+0,08	9,70	9,73	–0,03	22,06	22,07	–0,01
$C_{12}H_{20}O_2N_2Cu$	50,24		+0,18	9,66		–0,07	22,29		+0,22
Copper salicylalethylimine	60,10	60,07	+0,03	7,74	7,78	–0,04	17,44	17,65	–0,21
$C_{18}H_{20}O_2N_2Cu$	60,35		+0,28	7,62		–0,16	17,54		–0,11
Copper salicyalmethylimine $C_{16}H_{16}O_2N_2Cu$	57,79	57,91	–0,12	8,47	8,44	+0,03	19,04	19,15	–0,11

TABLE 6

Simultaneous Determination of Carbon and Silicon

Test material	C, %		Difference	Si, %		Difference
	found	calc.		found	calc.	
Octaethylcyclotetrasiloxane	47,08	47,00	+0,08	27,43	27,48	–0,05
$C_{16}H_{40}O_4Si_4$	47,22		+0,22	27,69		+0,21
Octamethylcyclotetrasiloxane	32,17	32,39	–0,22	38,03	37,88	+0,15
$C_8H_{24}O_4Si_4$	32,28		–0,11	37,94		+0,06
Tetrabutylsilane* $C_{16}H_{36}Si$	75,03	74,91	+0,12	10,73	10,95	–0,22
	74,74		–0,17	10,85		–0,10

Analysis of organosilicon compounds. During the combustion of these compounds, silicon is oxidized completely and remains in the form of a gel of silicic acid. 2% gelatine solution was added for precipitating and speeding up the filtration of the silicic acid from the sulfuric acid solution. Filtration, calcination, and weighing was carried out in porcelain crucibles with a porous bottom. When paper filters were used, considerable absorption of trivalent chromium salts was observed. In such cases it is necessary to wash the filter plus precipitate with hot hydrochloric acid (1 : 1).

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*In an atmosphere of pure oxygen, tetraethylsilane explodes when it comes into contact with the chromic mixture [7].

Table 6 contains examples of the analysis of some organosilicon compounds.

Since most chlorine-containing organosilicon compounds are readily hydrolyzed, aliquots of such liquid materials were taken in glass ampoules. Obviously, such a method is inapplicable to the gravimetric determination of silicon. The following technique was adopted for taking aliquots of readily hydrolyzable materials. Into a tared beaker containing a small amount of anhydrous sodium sulfate was introduced a few drops of the test material under an atmosphere of dry nitrogen, the beaker was then gently tapped so that the salt covered the sample; the whole was then weighed again in a closed weighing bottle. The technique of covering the sample with sodium sulfate was also used for the analysis of solid hygroscopic materials, or for the analysis of materials which are decomposed by concentrated sulfuric acid with evolution of gaseous products (e.g. hydrochlorides). The sodium sulfate acts purely as a sealer. During the analysis the salt dissolves and does not interfere with the subsequent determination of silicon or other elements.

The following results were obtained during the simultaneous determination of carbon, chlorine, and silicon in chlorophenyltrichlorosilane:

$C_6H_4Cl_4Si$ Found	C, %: 29.05;	Cl, %: 57.38;	Si %: 11.13
	29.20;	58.46;	11.23
Calculated	29.29;	57.65;	11.42

SUMMARY

A "wet" method has been developed for the simultaneous determination of carbon, halogens, and nitrogen in organic materials. The sample is heated at 150-160° with a mixture of concentrated sulfuric acid and a concentrated aqueous solution of chromic acid. The oxidation products are carried by a current of oxygen through a heated (700-750°) tube containing a catalyst – chromic oxide on pumice. Carbon is thereupon oxidized to CO_2. The latter is absorbed with ascarite and weighed. Halogens are isolated in the elemental state or in the form of the hydrogen halides. They are absorbed by an acetic acid solution of hydrazine hydrate and are titrated argentometrically by the Volhard Method. Nitrogen is determined after combustion by the Kjeldahl method.

Iron, copper, silicon and other elements which are mineralized during the oxidation process, and remain in the sulfuric acid solution, can be simultaneously determined with carbon, halogen, and nitrogen.

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NEW METHODS FOR THE QUANTITATIVE DETERMINATION OF HALOGENS IN ORGANIC MATERIALS. COMMUNICATION 4

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Earlier we pointed out [1] that organic materials which contain nitrogen and sulfur in addition to halogens cannot be analyzed by the new gravimetric method, since the nitrogen and sulfur oxides formed during decomposition react with the halogens, and thereby distort the results. Later we established that under certain conditions the nitrogen oxides do not appreciably affect potassium and sodium bromides (at temperatures of 680-700°). This fact made it possible to extend the methods described earlier for the determination of halogen to materials containing chlorine, bromine, and nitrogen, or chlorine, iodine, and nitrogen.

The percentage content of chlorine in a material is determined from the change in weight of an absorption tube packed with sodium or potassium bromide, while the chlorine and iodine content is determined from the difference between total halogens trapped at the exit of the tube, and the chlorine content already determined.

Trapping of the halogens at the exit from the first absorption tube was accomplished by means of slightly moist crystalline sodium carbonate and a solution of alkali and perhydrol (H_2O_2). This makes it possible to carry out a separate quantitative determination of chlorine and bromine, and of chlorine and iodine in materials containing nitrogen, and also carry out a quantitative determination of halogens, one at a time, in materials containing nitrogen and sulfur.

Decomposition of halogen-containing organic materials on heating in a stream of oxygen is always accompanied by the formation of a considerable amount of a mist containing the halogens, which is difficult to trap. This makes it necessary to carry out an analysis at moderate temperatures, with a great deal of care; nevertheless, this often does not guarantee complete absorption of the reaction products. We managed to overcome this difficulty by using filter tubes filled with fine crystalline powders of halide salts [1], this made it possible to carry out the combustion at a faster rate and at higher oxygen throughputs. Under these conditions, the halogens are readily, rapidly, and completely trapped; the absorbed halogen can be determined quantitatively by one of the known methods.

Decomposition of an organic material is strongly facilitated in the presence of chromic oxide as a catalyst [2]. Chromic oxide is, however, an active catalyst, accordingly it must be used with caution. Thus, in the presence of this catalyst combustion of an aliquot of the test material weighing 0.0500-0.1000 g is complete in 2-3 minutes.

Excess oxygen is necessary for ensuring complete oxidation of the test material.

Chromic oxide in the form of fine, pressed lumps, in a layer 100-120 mm long, is placed at the end of the combustion tube (constant packing) and is heated to 850-900°. Oxidation of test material which is not burnt in the boat is completed on the catalyst.

Simultaneous, separate, quantitative determination of two halogens (chlorine and bromine, or chlorine and iodine) in organic materials containing nitrogen. The apparatus is assembled as shown in Fig. 1.

Combustion is carried out in a tube of transparent quartz 15-20 mm in diameter and 750-800 mm long; the tube contains lumps (2-3 mm) of pressed chromic oxide kept in position at both ends by small plugs of asbestos fiber.

The first oven is heated to 750-800°; it serves for evaporating and partially burning the test material. The second oven serves for heating (800-900°) the catalyst.

Tube c is heated to 680-700°, the temperature being measured with a thermocouple. The outlet in the absorption tube c is closed with glass wool.

The hygroscopic cloud from the absorption tube is removed by heating it to 600-700° in the stream of oxygen passed through at a rate of 200-250 ml per minute.

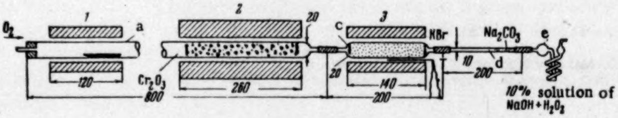

Fig. 1.

Tube d (200 mllong and 8-10 mm in diameter) is moistened with a 10% solution of alkali and perhydrol, excess of which is removed by slight shaking, after which one end of it is immersed in a supply of crystalline sodium carbonate, the tube being filled so as to give a layer 30-40 mm long.

3-5 ml of a 10% solution of alkali and 1.5-2 ml of perhydrol is introduced into the absorption apparatus e. The auxiliary apparatus is connected end to end to each other by means of rubber tubing 25-30 mm long. When the absorption tubes are properly packed, the oxygen should pass through freely at the rate of 200-250 ml/minute.

TABLE 1

Test material	Chlorine, %			Bromine, %		
	calc.	found	difference	calc.	found	difference
Polyvinylchloride Nitrobromobenzene	56,73	56,84	+0,11	39,55	39,48	−0,07
Polyvinylchloride Nitrobromobenzene	56,73	56,71	−0,02	39,55	39,61	+0,06
Dichlorobenzene Nitrobromobenzene	48,23	48,07	−0,16	39,55	39,53	−0,02
Dichlorobenzene Nitrobromobenzene	48,23	48,06	−0,17	39,55	39,32	−0,23
Hexachloroethane Dibromobenzene Nitrophenol	89,85	89,66	−0,19	67,75	67,68	−0,07
Hexachloroethane Dibromobenzene Nitrophenol	89,85	89,90	+0,05	67,75	67,46	−0,29

Analytical procedure. Test material is weighed out in a porcelain boat and strewn with a thick quartz sand or Cr_2O_3.

Volatile liquids are taken in capillaries. The boat is moved inside the combustion tube to a distance of 2-3 cm from the beginning of the first oven. By gradually moving oven 1 forward the material is evaporated or ignited.

In order to ensure uniform combustion, marks are made on the side of the tube at the place where the boat is located, at 5 mm intervals. Oven 1 is left in the same position for 3-5 minutes from the inception of combustion. Subsequently, at intervals of 30-60 seconds (depending on the character of the burning of the test material) the oven is moved forward.

Vapors of the test material plus its decomposition products are carried by the oxygen stream onto the heated zone where the catalyst is located; final decomposition takes place here.

During combustion, it is essential to keep the temperature of oven 3, in which the absorption tube c is located, constant.

When combustion is complete the oxygen is switched off. The contents of tube d and of apparatus e are quantitatively washed into the titration flask, while the absorption apparatus c is transferred to the balance room to cool. 3-4 ml of concentrated nitric acid is added to the titration flask and the whole boiled for 3-5 minutes. After cooling, 20 ml of 0.1 N silver nitrate is added to the contents of the flask, followed by 2-3 ml of ferric alum and excess silver nitrate back-titrated with potassium thiocyanate.

Since titrimetric determination is carried out more rapidly than gravimetric determination, we recommend working with two sets of absorption tubes.

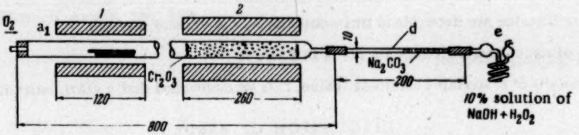

Fig. 2.

The second absorption apparatus d and apparatus e will contain the bromine from the sample and bromine liberated from the first absorption apparatus c; the amount of bromine in the sample will be equal to the total amount of bromine which has passed into the absorption tube d minus the amount of the bromine liberated by the chlorine from the first absorption tube c.

Results for the determination of chlorine and bromine are given in Table 1.

TABLE 2

Test material	Halogen, %		
	calc.	found	difference
Dichlorobenzene Thiourea	48,23	47,98	—0,25
Dichlorobenzene Thiourea	48,23	48,21	—0,02
Nitrobromobenzene Sulfosalicylic acid	39,55	39,31	—0,24
Nitrobromobenzene Sulfosalicylic acid	39,55	39,51	—0,04
Dichlorobenzene Nitrocinnamic acid	48,23	48,18	—0,05
Dichlorobenzene Nitrocinnamic acid	48,23	48,19	—0,04
Nitrobromobenzene	39,55	39,45	—0,10
Nitrobromobenzene	39,55	39,33	—0,22
Bromaniline	46,45	46,20	—0,25
Bromaniline	46,45	46,47	+0,02
Bromacetanilide	37,33	37,16	—0,17
Bromacetanilide	37,33	37,34	+0,01
Nitrochlorobenzene	22,50	22,45	—0,05
Nitrochlorobenzene	22,50	22,36	—0,14

Materials containing chlorine and iodine. The iodine trapped in tube d and apparatus e can be determined quantitatively by one of the published methods, for example by the Leipert method [3].

Quantitative determination of halogens (chlorine, bromine, or iodine) in organic materials containing nitrogen and sulfur.

The analysis is carried out in the apparatus shown in Fig. 2.

The use of chromic oxide as a catalyst cuts down the time for an analysis to 20 minutes.

Absorption of halogens by means of moistened crystalline sodium carbonate and a solution of alkali and perhydrol makes it possible to determine halogens in the presence of nitrogen and sulfur.

The absorption tube d can be connected directly to the combustion tube. A lengthened layer (100-120 mm) of crystalline, slightly moist sodium carbonate serves both as a filter and as an absorber.

For titrimetric determination it is recommended that the test material in the boat be sprinkled with chromic oxide.

The rest of the analytical procedure is the same as that described above.

Chlorine or bromine are determined titrimetrically by the Volhard method.

Examples of some determinations are given in Table 2.

For the analysis of materials containing iodine, it is recommended that a gravimetric finish be used.

DISCUSSION OF RESULTS

Existing techniques and methods for the quantitative, separate determination of several halogens on one aliquot of organic material possess a number of drawbacks. They take a long time to carry out, they are difficult, demand a number of operations, and the expenditure of expensive reagents (silver, platinum, etc.). The new method which we have developed makes it possible to carry out the separate, quantitative determination of two halogens (chlorine and bromine, or chlorine and iodine) in organic compounds containing nitrogen.

It has been established that under the experimental conditions we used, at a temperature of 600-700°, potassium (sodium) bromide does not react with nitrogen oxides, since the equilibrium recction $2NO_2 \rightleftharpoons 2NO + O_2$ is strongly shifted towards formation of the little-active nitric oxide under these conditions. On issuing from the heated absorption tube c, however, nitric oxide is readily oxidized to nitrogen peroxide which thereupon reacts with the damp potassium iodide. Accordingly, we replaced potassium iodide by crystalline sodium carbonate and a solution of alkali and perhydrol. We also used sodium bisulfate for this purpose as well as crystalline sodium carbonate; the results were promising. Other crystalline salts could probably be used for filling tube d. The filler in tube d plays the part of a filter for removing the mist formed and also as an absorbent for the halogens.

Before titrating with potassium thiocyanate, nitrogen oxides should be removed from the solution by boiling.

For a gravimetric finish during determination of chlorine, about 25-30 g of bromide is required for one filling of the heated absorption tube c. This amount of bromide is sufficient for more than fifty analyses for sample weights of 0.0500-0.1000 g. The success of an analysis depends to a very large extent on observance of a constant temperature in the absorption tube.

The methods described can be successfully used for analyzing organic compounds containing both mobile and immobile halogens. The method permits combustion of large aliquots, or of a series of aliquots, by passing the decomposition products through the same absorber; this means that it is possible to determine small amouts of halogen in test materials. The experimental error is ± 0.1-0.3%.

A gravimetric determination takes 50-60 minutes, while a titrimetric determination takes 20-30 minutes.

SUMMARY

Chromic oxide has been used as a catalyst for facilitating combustion of test material. The mists formed during the decomposition of test halogen-containing materials, are destroyed by means of finely powdered

crystalline sodium carbonate or sodium bisulfate, with equal success to that obtained with the halogen salts tested previously.

It has been demonstrated that it is possible to carry out a simultaneous, separate determination of chlorine and bromine, or chlorine and iodine in organic materials containing nitrogen.

A method is described for the determination of chlorine, bromine, or iodine in organic materials containing nitrogen and sulfur.

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RAPID METHODS OF MICROELEMENTAL ANALYSIS

COMMUNICATION 16. THE RELATION BETWEEN THE LENGTH OF THE CONTACT LAYER AND THE METHOD OF DECOMPOSITION* DURING THE DIRECT DETERMINATION OF OXYGEN

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During the last fifteen years an important event in the development of microelemental analysis was the solution of the problem of the direct determination of oxygen. Published literature reviews illustrate how this problem, which was the object of an intense effort on the part of many chemists in the course of more than one hundred years [1-3], developed. The essence of the method generally accepted at the moment for the direct determination of oxygen is the thermal decomposition of the test material in a stream of pure nitrogen, the conversion of all the oxygen into CO over carbon which has been heated to 1100-1120° [4-6] or 1150° [2, 7, 9], and the subsequent oxidation of the CO into CO_2 which is then determined gravimetrically or titrimetrically.

Up to 1947 direct determination of oxygen was carried out only in Germany [4-6] and in the Soviet Union [2, 7, 9]. The method then widely entered into analytical laboratory practice in America [10-16] and Europe [17-22]. During recent years much work has been published on the direct determination of oxygen in various materials: in organic compounds [2, 4-7, 14, 19], coal [23-29]; in rubber, resin, gutta percha, petroleum products and asphalt [30-32, 11] and in inorganic materials [2, 4, 6, 33]. The method for the direct determination of oxygen has already found its place in the textbooks on quantitative organic microanalysis [9, 34-37].

Naturally, during such wide application, the method has been studied in detail by many analysts and many modifications and improvements have been made. Workers who have worked on improving the method have turned their attention to: 1) the preliminary purification of the inert gas used (nitrogen or helium) and to improvements in this technique [4-6, 9, 13, 14, 15, 21-22, 30]; 2) studying the sources of error connected with the quality of the quartz [14, 19-22, 34, 39-42]; the carbon [2, 4, 9-14, 18-19, 21, 43-47] and the iodine pentoxide [13, 38, 43-45, 48-51] used; and 3) to looking for a better way of determining the CO [11-12, 14, 19, 21-22, 27-28, 30, 46, 52-56]. Nevertheless, questions touching on the relation between the optimum value of the contact layer and the method of decomposing the test material have not yet been considered. The present article is devoted to this question.

From the experience gained in our laboratory on the determination of carbon and hydrogen, and the simultaneous determination of C and H and other elements, it has been established that preliminary pyrolysis of the test material facilitates quantitative oxidation [9, 57-61] as well as reduction [9, 62-63] of the aliquot considerably, as a result of which, it is not the vapors of the test material, but the active products of its decomposition, which are subjected to oxidation or reduction. Decomposition can be carried out in a similar manner during the determination of oxygen as well.

When the sample is placed in a quartz test tube and it is pyrolytically decomposed (i.e., the test tube is heated along the direction from the open end towards the closed end with an oven or with a burner) and the material is not evaporated from the boat, as is usually done by all workers working on the direct deterimination of oxygen, then one might expect that the decomposition products issuing from the test tube will, undoubtedly, be much more reactive than the vapors of the undecomposed material, and will react considerably more easily than the latter with the contact layer of carbon at 1150°. Thanks to this a much shorter layer of carbon will be sufficient than that hitherto used. In order to convince ourselves of the efficiency of such a method of decomposition for the determination of oxgen, we carried out pyrolytic decomposition of the sample placed in a quartz test tube contained in an empty tube used for the decomposition, pure and dry nitrogen being passed through at the rate of 10-12 ml/minute. Since no carbon contact layer was present in the tube, the oxygen came off as water, carbon monoxide, and carbon dioxide. The carbon monoxide was oxidized to carbon dioxide over cupric oxide at 100° and the oxygen-containing products determined by weight. It was established in this way that during preliminary pyrolysis of an organic material carried out in a quartz test tube at 900-1000°, in an atmosphere of pure nitrogen, the tube used for decomposition being empty, the total percentage of oxygen calculated on the basis of the water and the carbon monoxide and dioxide amounts to 90% of the total content of oxygen in the test material (Table 1). Accordingly, when the method described above is used for decomposition, a considerable break down of the test organic material can be achieved. The fact that some of the oxygen is not accounted for can probably be ascribed to the presence of oxygen containing fragments of the molecule in the decomposition products.

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**Deceased.

TABLE 1

Test material	Weight of sample,mg	Oxygen found in the form of, %			Total oxygen found, %	
		H_2O	CO	CO_2	absolute	relative
Saccharose	5,509	30,98	7,86	7,31	46,15	89
$C_{12}H_{22}O_{11}$, 51,42% O	5,983	29,76	7,08	7,60	44,44	86
Salicylic acid	4,876	4,83	20,32	4,01	29,16	84
$C_7H_6O_3$, 34,75 % O	5,028	7,21	19,11	2,69	29,61	84
γ-Methyl glucoside	5,710	16,80	5,83	7,27	29,90	59
$C_7H_{14}O_6$, 49,44 % O	5,959	17,96	4,58	8,24	30,78	61
Benzoic acid	4,450	2,57	22,25	0,17	24,99	95
$C_7H_6O_2$, 26 20 % O	4,437	2,32	21,56	0,55	24,43	93
Cis-4-ketocyclohexanedicarboxylic acid	4,689	2,45	20,31	15,58	38,44	89
$C_8H_{10}O_5$, 42,97 % O	5,063	2,33	22,57	16,04	40,94	94

TABLE 2

Test material	Wt. of sample, mg	% O		Experimental conditions
		found	difference	
Saccharose	12,240	51,28	−0,14	Length of the contact layer of granulated carbon 5 cm, temperature 1150° Nitrogen throughput 10-12 ml/minute Decomposition of test material was carried out in a quartz test tube 7 cm long using a gas burner
$C_{12}H_{22}O_{11}$, 51,42 % O	12,134	51,53	+0,09	
Salicylic acid	13,745	34,56	−0,19	
$C_7H_6O_3$, 34,75 % O	11,371	34,76	+0,01	
Cis-4-ketocyclohexanedicarboxylic acid	4,025	42,87	−0,16	
$C_8H_{10}O_5$, 42,97 % O	3,471	43,09	+0,12	
Dimethyl ester of azobenzoic-3,3'-dicarboxylic acid	8,497	21,37	−0,10	
$C_{16}H_{14}O_4$, 21,47 % O	8,486	21,42	−0,05	
Urea	9,585	26,69	+0,03	
CH_4ON_2, 26,66 % O	11,491	26,60	−0,06	

Experiments were then carried out with a shortened layer of carbon in the decomposition tube. A layer of granulated carbon 5 cm long was placed in the quartz tube and heated to 1150° (± 20°) with a tubular oven 10 cm long. The aliquot was introduced into the tube in a quartz test tube 7 cm long; the latter was placed at a distance of 5-6 cm from the oven. The test tube was intially heated with a gas burner at the open end in the same way as for the determination of carbon and hydrogen [9, 57-63]. The gaseous decomposition products, on issuing from the test tube, were carried along with the nitrogen flow into the contact layer of granulated carbon heated to 1150°; here, all the oxygen contained in the vapor was quantitatively converted into carbon monoxide. The latter was oxidized to CO_2 by means of cupric oxide, the CO_2 being finally trapped with ascarite. The results obtained showed that the accuracy of the determination of oxygen in organic materials when the contact layer of carbon is shortened to 5 cm (Table 2) is adequate.

As our further experiments showed, determination of oxygen in organic compounds can also be carried out in an empty tube, when the contact layer of carbon is placed directly in the quartz test tube over the sample itself. A micro electric burner 6 cm long was used for heating the test tube at 1150°. By moving the burner slowly forward from the open end of the test tube towards the closed end, quantiative conversion of the oxygen in the sample to carbon monoxide was achieved in the test tube itself. The CO was subsequently oxidized as described above. Results of analyses carried out by this technique are given in Table 3.

TABLE 3

Test material	Wt. of sample, mg	% O		Experimental conditions
		found	difference	
Saccharose	6,601	51,25	−0,17	The contact layer of granulated carbon 5 cm long was placed in a quartz test tube 9 cm long. Decomposition was effected with a micro electric burner 6 cm long at 1150°.
$C_{12}H_{22}O_{11}$, 51,42 % O	11,023	51,24	−0,18	
Benzoic acid	6,930	26,17	+0,03	
$C_7H_6O_2$, 26,20 % O	5,962	26,45	+0,25	
α, α, β-methyl ester of naphthalenetricarboxylic acid	9,432	31,01	−0,14	
$C_{16}H_{20}O_6$, 31,15 % O	8,593	31,00	−0,15	
2, 2-Dimethyl-3-di-β-cyanethylpyrone	8,397	13,49	−0,18	
$C_{13}H_{16}O_2N_2$, 13,67% O	9,049	13,65	−0,02	
Uric acid	7,905	28,62	+0,05	
$C_5H_4O_3N_4$, 28,57 % O	7,481	28,72	+0,15	

These experiments showed that by adopting preliminary pyrolysis of the test material in a quartz test tube, there is no need for a long contact layer of carbon. When the above technique is used, a carbon layer 5 cm long can be used instead of a 16-20 cm long layer. When this method is adopted, the carbon can be placed either in the decomposition tube or directly in the test tube containing the test sample. Accordingly, there is no need for a long tube for carrying out the decomposition, and it is possible to work with a tube which is only 30 cm long instead of 50 cm. Experiments which we have carried out in an empty tube, the carbon being placed inside the test tube used for decomposition, give a basis for hoping that in future it will be possible to cut down the length of the contact layer even more. The use of platinized carbon [63-65] made it possible for us to lower the temperature to 900°. A separate article will be devoted to this work.

SUMMARY

It has been established that during the pyrolytic decomposition of material in a nitrogen atmosphere in a quartz test tube placed in an empty quartz tube, almost quantitative decomposition of the sample occurs, during which up to 90% of the oxygen is liberated as H_2O, CO, and CO_2.

Preliminary pyrolysis of the sample considerably facilitates quantitative formation of carbon monoxide, so that it is possible to cut down the length of the contact layer, and, accordingly, also cut down the length of the reaction tube.

It has been shown that it is possible to determine oxygen using an empty tube for decomposing the sample, the carbon layer being enclosed in the same quartz test tube as the sample itself.

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QUANTITATIVE DETERMINATION OF THE THREE NITROCHLOROBENZENE ISOMERS IN THEIR MIXTURES BY MEANS OF THEIR INFRARED ABSORPTION SPECTRA

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Analysis of mixtures of isomeric organic compounds, in particular, in the aromatic series of position isomers, is often a very difficult problem; as a result of the similarity of the properties of like isomers, the chemical, and also the most widely used physicochemical methods of analysis rarely achieve their ends. The most promising technique for aromatic isomers would appear to be the use of vibration spectra, in particular, infrared absorption spectra. The spectra of isomers usually differ considerably from each other, and can be used for analytical purposes.

Technical nitrochlorobenzene, both as a primary nitration product, and the various fractions obtained during successive distillations and crystallizations, are mixtures of the ortho and para isomers in varying amounts together with a small amount of meta isomer.* The usual method used for analyzing these products is doubly approximate. The ratio of the o- and p-isomers is established from the setting point, while the presence of the m-isomers is disregarded. The latter is determined bromometrically after reduction of the nitro group. This method is an indirect method, since all the three isomers use up bromine (the o- and p-isomers 4, and the m-isomer 6 atoms). The present article contains a description of the direct determination of the m- and p-isomers by means of their infrared absorption spectra; the amount of the o-isomer is determined by difference.

The spectra of the materials under discussion have already been studied [1], but in a narrower frequency range (500-1200 cm^{-1}) and without any emphasis on their possible analytical application. Within the range just indicated our results are in good agreement with published data [1].

EXPERIMENTAL

Apparatus. The infrared absorption spectra were obtained on an IKS-11 single-beam instrument, the amplifying-recording setup of which was modified considerably. While not differing essentially from the setup described previously [2], it was better designed from the point of view of selecting the operating conditions.

The photorelay with a high ohmic output is the first branch of a new recording system, and was achieved by simple redesigning of the FÉOU-15, as described in [2]; this was carried out as follows: the FÉSS-10 photoelement in the second cascade of the FÉOU-15 was replaced by STsV-4 vacuum photoelements. By substituting the first input galvanometer (coil resistance 12 ohms, redamped operation, sensitivity of 0.53×10^{-7} amps/mm/m) which is the most sensitive to noise, by a third (output) galvanometer (coil resistance 200 ohms, redamped operation, sensitivity of 1.42×10^{-6} amps/mm/m) the noise level was cut down. By making similar changes the amplifying factor of the photorelay was reduced, the photorelay is given the role not of an amplifier, but of a convertor of the signal from the low-ohm circuit of the thermoelement ($R_{T.E.}$ = 11.07 ohms) into the high-ohmic circuit of the vacuum photoelements ($R_{T.E.}$ is equal to several hundred megohms).

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*It is only by using very efficient distillation columns that it is possible to isolate a fraction containing an appreciable amount of the m-isomer.

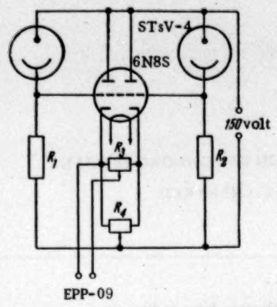

Fig. 1. Operating scheme of the cathodic repeater.

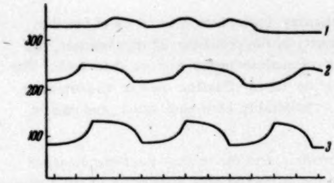

Fig. 2. An example of recordings of weak signals; 1) 1×10^{-8} volt; 2) 2×10^{-8} volt; 3) 3×10^{-8} volt; (the whole scale of ÉPP-09 covers 15 millivolts).

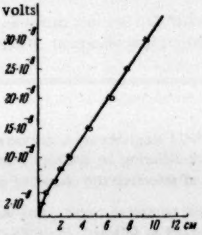

Fig. 3. Curve relating readings of the recording ap- apparatus (in cm) to the signal strength at the amplifier input (in volts).

It is known [3] that cathodic amplification can be relatively simply applied to signals in the high-frequency circuit of vacuum photoelements. It has been established [2] that a cathodic repeater is particularly suitable for this purpose [4].

The differential cathodic repeater (operating scheme) is shown in Fig. 1. The parameters of the dc current in the photometric setups are chosen with regard to the sensitivity and internal resistance of the recording apparatus. The latter was a ÉPP-09 electronic self-recording potentiometer, i.e. an apparatus with a low output resistance; thereby it was possible to get some freedom of choice for the loading resistance (R_L) in the cathodic repeater circuit. The cathodic resistance R_C should be considerably greater than the load resistance for the greater slope of the amplifier. The basic parameters of the operating scheme of the cathodic repeater were as follows: $R_1 = R_2 = 22$ megohm, $R_3 = R_4 = 3$ kilohms , $R_C = 20$ kilohms. A double triode 6N8S with the parameters $\mu = 25$, $s = 4$ milliamp/ / volt was used (for a filament voltage of 6.3 volt and an anodic voltage of 240 volts).

The zero drift, in principle, is depressed largely due to the presence in the scheme of a strong negative back coupling (feedback) [4]. Low values of the supply voltage are also essential for zero stability. Special attention must be given to this point, otherwise it will be impossible to achieve satisfactory zero stability, even when stable supply sources are used such as NKN-45 accumulators, and BSG-70 high-frequency batteries on which our amplifier worked. Finally, it is important that the scheme should have the minimum number of control details. The choice of tubes and photoelements operating in the setup is not complicated; the only requirement is that the parameters in both halves of the triode should be equal to one another to within one percent, and that the sensitivities of the photoelements operating in pairs should be equal to within three percent; such a requirement is usual for elements of a balance scheme.

The operating conditions for the amplifying-recording system which were chosen experimentally were as follows: voltage of the filament of the tube of the photorelay lighting 1.6 volt; filament voltage of the electronic tube 5.9 volt; anode voltage and voltage on the SPV-4 photoelements = 150 volts. During the calibration of the scheme, the following indices were obtained: dark current of the photoelements 2.4×10^{-10} amps; current 13×10^{-8} amps; grid current of the tube 1×10^{-9} amps; anode current 1.4 milliamp; sensitivity of the whole setup 2×10^{-8} volt; amplification factor 2×10^4; zero drift 0.7 millivolt/hour; time constant about 10 seconds. In Fig. 1 are given examples of records of weak signals which give an idea of the sensitivity and the amplification factor of the new amplifying-recording system. An important property of the scheme is its good linearity at signals $\geq 4 \times 10^{-8}$ volt; this is illustrated in Fig. 3.

On the whole, the recording system which is characterized by maximum simplicity of preparation and control, ensures accurate and convenient recording of the spectra by means of a pen.

Automatic recording of spectra on the setup described above is completely satisfactory for the purposes of qualitative study of spectra, for identification of materials, etc. For the case of the quantitative analysis of mixtures, which is based on measurements of intensity, the small zero drift which occurs, as well as the insufficient constancy of the source of the infrared radiation, lead to an increase in experimental error. In this case, therefore, in order to measure the intensity of the "key" absorption bands we took readings on the basis of points as follows. First of all with the potentiometer covered from the radiation, a zero reading was taken; the radiation was then switched on, the solvent introduced into the beam and the "100% transmission" (I_0) reading taken. The zero reading was repeated and then the sample placed in the beam and the reading (I) taken. The transmission (in %) is given by the expression $T = I/I_0 \times 100$.

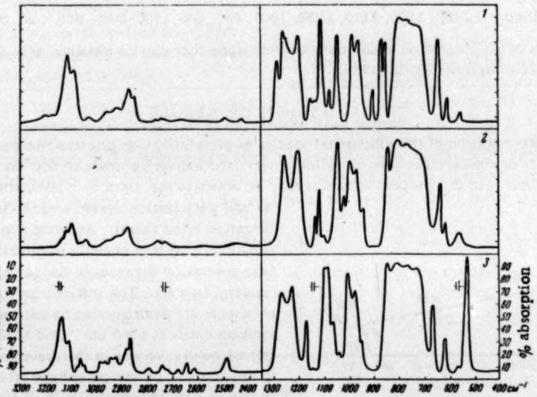

Fig. 4. Infrared absorption spectra of solutions of monochlorobenzene isomers: $l = 0.507$ mm; 1) m-isomer (molar fraction 0.03070); 2) o-isomer (0.03058); 3) p-isomer (0.03079).

Test materials. The following materials were studied: m-nitrochlorobenzene, m.p. 43.5°; p-nitrochlorobenzene m.p. 33.9°; p-nitrochlorobenzene, m.p. 82.8°. These materials were prepared by purification (recrystallization) of industrial products. The solvent used was carbon tetrachloride, b.p. 75.0° (775 mm Hg); n_D^{20} = 1.4620; this was obtained by washing, drying, and distilling the industrial product.

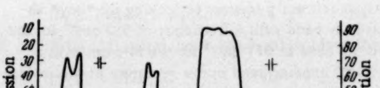

Fig. 5. Infrared spectrum of the solvent (l = 0.507 mm).

Experimental results. The infrared absorption spectra of solutions of the nitrochlorobenzene isomers were taken over the ranges 100-1300, 2400-3300 cm^{-1}.* During the work in the spectral regions chosen, interchangeable prisms of potassium bromide, rock salt, and lithium fluoride were used. The spectral slit width in the 400-650 cm^{-1} region, was about 11 cm^{-1}, in the 650-1300 cm^{-1} region about 8 cm^{-1}, and at

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*Absorption spectra in the 1300-2400 cm^{-1} region were not studied for the reason that in this region there is considerable absorption by water vapor; this would have made it impossible, or, at least, very difficult to carry out analytical work without additional constructional modifications to the spectrometric setup.

3000-3300 cm^{-1} it was equal to about 7 cm^{-1}.*

In Figs. 4 and 5 are given the spectra of the solutions and also of the solvent in the region where its selective absorption occurs (corrected for the scattered radiation of the high frequencies in the spectrometer).

The values of the frequencies which were measured with an accuracy of ± 3, ± 5 cm^{-1} were as follows;

Meta-nitrochlorobenzene:: 3220, 3183, 3130, 3040, 2975, 2930, 2885, 2867, 2780, 2755, 2740, 2510, 2443, 1297, 1270, 1160, 1150, 1125, 1093, 1063, 917, 879, 867, 657 cm^{-1};

Ortho-nitrochlorobenzene: 3145, 3127, 3105, 3050, 2885, 2770, 2785, 1142, 1127, 1053, 1030, 950, 848, 647 cm^{-1};

Para-nitrochlorobenzene: 3135, 3105, 3070, 3060, 3045, 2980, 2920, 2876, 2865, 2793, 2737, 2693, 2673, 2640, 2610, 2483, 1175, 1105, 1090, 1040, 1013, 953, 846, 675, 533 cm^{-1};

Carbon tetrachloride: 1263, 1220, 1113, 1070, 1007, 980, 945, (700-800), 665, 623, 568 cm^{-1}.

The intensities of the absorption bands are not given since they can be obtained with the requisite accuracy (3% absolute) from the corresponding diagrams.

DISCUSSION OF RESULTS

A complete interpretation of the vibrational spectra of such fairly complicated molecules as those of nitrochlorobenzene, is of considerable theoretical difficulty, and cannot be made on the basis of the infrared absorption spectra alone. For this purpose attention may be drawn to the data on combination scattering spectra and polarization measurements (see [6, 7] and the literature cited there). According to our experimental results (Fig. 4) it is possible to establish the characteristic spectral differences in the series of nitrochlorobenzene isomers. The infrared spectra of the m- and o-isomers are distinguished by narrow and strong absorption bands at 1063 cm^{-1} and 1053 cm^{-1} and such an intense band is absent in the spectrum of the p-isomer in this region; on the other hand, there is a very intense and very characteristic band with a frequency of 533 cm^{-1}. In turn there is a band with a frequency of 917 cm^{-1} in the spectrum of the m-isomer. Despite the fact that this band is of low intensity, nevertheless, it can serve as a qualitative characteristic for the m-isomer, since the two other isomers do not generally have an absorption band in this region. The band at 879 cm^{-1} is also very characteristic for the m-isomer.

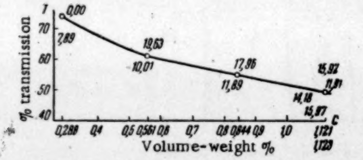

Fig. 6. Calibration curve for m-isomer: Figures on the left-concentration of p-isomer; figures on the right- concentration of o-isomer.

The observed spectral differences of the three isomers considered here are quite sufficient for recognizing them in their mixtures. The problem of quantitative analysis primarily reduces to looking for "key" absorption bands. Obviously there is no doubt that one can regard the band with a frequency of 533 cm^{-1} for the p-isomer as a "key" band. It might also be possible to regard the band at 917 cm^{-1} for the m-isomer as a "key" band, if it had a greater intensity. In addition to this band, another band in the spectrum of the m-isomer which attracts attention is the 879 cm^{-1} band, although there is a danger that this band is not free from superposition from the bands at 848 and 846 cm^{-1} of the o- and m-isomers, which are fairly close. By decreasing the spectral width of the slit** to 4 cm^{-1} we were able to destroy completely the bands at 879 and 867 cm^{-1} of the m-isomer, while a check on the superposition of the 879 cm^{-1} band by the 848 and 846 cm^{-1} band in this case, showed that for contents of 0.5-3% of the m-isomer in the mixtures, the experimental error in its determination did not exceed 10% (relative). When the m-isomer content of the mixture is greater than 5%, the experimental error is only determined by errors in the measuring setup and amounts to (for measurements of of the intensity of the absorption bands on the basis of points) about 1% (relative). A detailed check established that the absorption band at 533 cm^{-1} for the m-isomer is completely free from superposition by the bands of the other isomers.

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*The spectral slit width was calculated by means of the formula generally accepted for infrared prism spectrometers, see [5].

**This decrease in slit width did not lower the accuracy of measurements of absorption band intensity in our setup.

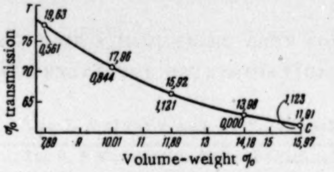

Fig. 7. Calibration curve for the p-isomer: Figures on the left – concentration of the m-isomer; figures on the right – concentration of o-isomer.

Thus, the bands at 879 and 533 cm^{-1} can be regarded as "key" bands, and direct determination of the m- and p-isomers in their mixtures is possible by means of them. For this purpose calibration curves were constructed (Figs. 6 and 7), T = f(C), where C is the volume-weight concentration, T is the percentage transmission at 879 cm^{-1} (or 533, respectively) in the spectrum; t is measured with an accuracy of 1%. The calibration curves shown in Figs. 6 and 7 were only obtained for mixtures of all three isomers in order to show graphically the insignificant superposition of the "key" absorption bands on other bands which are located close to them in the spectrum. For practical work it is sufficient to construct calibration curves for solutions containing just that isomer which it is desired to determine in a given mixture, since the experimental error has already been studied.

The percentage content of the isomers in a sample is calculated by means of the formula: % isomer = P·V/g, where P is the percentage of the isomer in solution, found from the calibration curve constructed on the basis of the measured transmission (T), V is the volume of the solution, and g is the weight of sample.

SUMMARY

A method has been developed for the quantitative determination of the m- and p-isomers in technical nitrochlorobenzene. The lowest content determined is about 0.5%; the experimental error varies within ±1 and ±10% (relative).

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BRIEF COMMUNICATIONS

THE USE OF A "SOUNDING ARC" FOR INCREASING THE REPRODUCIBILITY OF QUANTITATIVE DETERMINATIONS IN SPECTROGRAPHIC ANALYSIS

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An essential drawback of a dc arc, which ensures comparatively high sensitivity during spectrographic determination, is the relatively low reproducibility and stability of the evaporation conditions of the elements, and of the excitation of their atoms. In order to increase the reproducibility of quantitative spectrographic determination of elements, and to increase the accuracy, use is made of a dc impulse arc [1]. Another possibility is, apparently, the use of a so-called "sounding" (Schallbogen) arc, which has already found use in radiotechnics [2] for obtaining undamped electromagnetic vibrations. The scheme of such an arc is shown in Fig. 1. The principle of its operation is as follows. It is known that the arc plasma which is included in the electrical circuit does not possess constant resistance. As a result of this the direction of the current on the electrodes changes continuously. When the arc is connected in an oscillating circuit (Fig. 1), the period of the characteristic vibrations of which is $T = 2\pi\sqrt{LC}$, then the vibration of the plasma will increase with this period, and in its turn will interact so as to increase the intensity of the vibration of the circuit. Under such conditions one should expect some stabilization of the arc discharge at a frequency $\omega = 1/T$, and an increase in stability of the working conditions of the arc following upon this. Outwardly, this is manifested by the arc beginning to sound when ω lies within the limits 50-20,000 cycles. In order to prevent the alternating component of the arc from shunting into the main circuit, and from being shunted by the current source, a large self-inductance L_1 is introduced into the circuit.

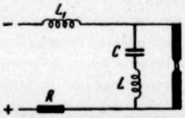

Fig. 1. Schematic diagram of a "sounding" arc.

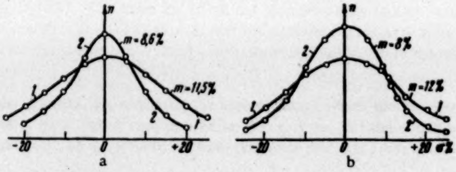

Fig. 2. Comparison of the curves for the distribution of errors during quantitative determination of hundredths of a percent of antimony (a), and whole percentages of gallium (b) in uranoso-uranic oxide by the Scribner-Mullin method [3]: 1) In the normal type of dc arc; 2) in a "sounding" arc.

An experimental check on the possibility of increasing the stability of the operating conditions of a dc arc by including it in the setup for a "sounding" arc gave encouraging results. As is evident from the curves

(Fig. 2), the distribution of errors in the case of excitation in a "sounding" arc, despite the rather crude way in which the experiments were carried out, is characterized by a smaller value for the standard error than when excitation is carried out in the normal type of dc arc.

More detailed information regarding the possibilities of a "sounding" arc in spectrographic analysis will be published later, after completing the investigation.

SUMMARY

The use of a "sounding" dc arc is suggested for increasing the reproducibility of the spectrographic determination of elements.

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SPECTROGRAPHIC DETERMINATION OF BISMUTH, CADMIUM, TIN, LEAD AND ANTIMONY PRESENT AS IMPURITIES IN TANTALUM

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Production of high-purity tantalum has required the development of methods for determination of bismuth, cadmium, tin, lead, and antimony present as impurities in it. The permissible content of each of these impurities should not exceed $1 \times 10^{-4}\%$. It is clear from this that any method of quantitative analysis used should possess a sensitivity of $3 \times 10^{-5}\%$.

In order to overcome the difficulties arising during the spectrographic analysis of tantalum metal (the difficulty of preparing homogeneous standards from tantalum, possible liquefaction in the test sample, etc.), it is convenient to convert the metal into its oxide, the impurities being then determined in the latter.

In developing an analytical technique it was borne in mind that tantalum pentoxide is a relatively nonvolatile oxide, while the oxides of the five impurity metals to be determined are relatively volatile. This gave us grounds to hope that the evaporation method [1, 2] would be the most efficient method. In actual fact, the use of this method enabled us to achieve the necessary sensitivity for the determination of these five impurities in tantalum, the sensitivity in this case being higher than the sensitivity achieved by means of a dc arc [3].

The tantalum was oxidized by heating it in a muffle furnace at a temperature of 600-700° for 1.5-2 hours. The agreement between the results of spectrographic analysis of three samples of tantalum oxidized by two different methods: 1) by calcining the metal in a muffle furnace; 2) by dissolving the metal in a mixture of nitric and hydrofluoric acid, by repeated evaporation of the solution containing nitric acid, and finally calcining the precipitate to the oxide, indicates the absence or loss of impurities on calcining the metal to pentoxide in a muffle furnace at a temperature of 600-700° (Table 1).

In order to choose the temperature at which the samples of tantalum pentoxide can be heated so as to ensure complete or reproducible evaporation of the impurities, without evaporating the main component of the sample, the impurities were evaporated from 100 mg aliquots of the same sample at various temperatures starting at 900 and finishing at 1600°. The time for which the aliquots of the sample were heated was one minute. The experimental results indicated (Table 2) that the optimum temperature for heating the sample is 1400°. Using these conditions, the impurities studied evaporate completely, while the main component (Ta_2O_5) is hardly evaporated at all.

Copper was used as the material for preparing the electrodes on which the evaporated impurities were condensed. Spectrographically pure carbon can be used for this purpose, but the experimental accuracy in this case is almost halved. Distillation of the impurities from tantalum pentoxide was carried out in carbon crucibles.

The internal standard method was used for achieving reproducible results. The internal standard used was thallium which was added to test samples and standards in amounts of $1 \times 10^{-2}\%$. The analytical pairs of lines used are given in Table 3.

The suitability of the analytical pairs of lines chosen for the determination was checked by changing the interelectrode gap, and the self-inductance of the spark generator.

The spectra of the impurities condensed on the electrodes were excited by means of a condensed spark discharge from a IG-2 generator (simple scheme, L = 0.15 microhenries, C = 0.01 microfarads).

The value chose for the analytical gap was 2 mm, since for this value the maximum blackening of the analytical lines was observed.

TABLE 1

Effect of the Method used for Oxidation on the Analytical Results

Content of impurity, %							
Calcining in air				Dissolution in acids			
Bi	Cd	Sn	Pb	Bi	Cd	Sn	Pb
$8,5\cdot10^{-5}$	—	$2,0\cdot10^{-3}$	$8,7\cdot10^{-4}$	$8,0\cdot10^{-5}$	—	$1,9\cdot10^{-3}$	$9,0\cdot10^{-4}$
$5,0\cdot10^{-5}$	$4,2\cdot10^{-5}$	—	—	$4,8\cdot10^{-5}$	$4,4\cdot10^{-5}$	—	—
$3,8\cdot10^{-6}$	—	—	—	$4,0\cdot10^{-5}$	—	—	—

An ISP-22 quartz spectrograph was used for the work. The spectra were photographed on "spectrographic type III" plates. Exposure time was 10 seconds.

Tantalum pentoxide free from the impurity elements being determined was used for preparing standards. A check on the "purity" of the base material was carried out by the method of addition. The impurity elements were introduced in the form of solutions of their nitrates, while tantalum was introduced in the form of its sulfate. The mixture obtained was calcined for one hour at 500° and then ground up in a mortar. The remaining standards were prepared by diluting this stock standard with pure base material.

TABLE 2

Relation between the Blackening of the Analytical Lines of the Impurities and the Temperature at which the Tantalum Pentoxide is Heated*

Temperature (°C)	Blackening				
	Bi	Pb	Sn	Cd	Sb
900	0,25	—	—	0,32	—
1000	1,28	0,21	—	1,33	—
1100	1,65	1,15	—	1,54	—
1200	1,82	1,68	0,34	1,85	0,36
1300	1,80	1,72	0,80	2,05	0,85
1400	1,92	1,92	1,36	2,00	1,49
1500	1,77	1,85	1,35	1,95	1,41
1600	1,80	1,95	1,32	2,00	1,42

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*The analytical lines of the impurity elements given in Table 3 were used. The most intense lines for tantalum appear on the spectro grams when the samples are heated at 1500°.

TABLE 3

Analytical Pairs of Lines

Element	Analytical line A	Excit. potential elec.volts	Reference line, A	Excit. potential elec.volts	Concentration range, %
Bi	3067,72	4,0	Tl 2918,32	5,2	$1\cdot10^{-5}-1\cdot10^{-3}$
Sn	2839,99	4,8	Tl 2918,32	5,2	$3\cdot10^{-6}-1\cdot10^{-3}$
Pb	2833,07	4,4	Tl 2918,32	5,2	$3\cdot10^{-6}-1\cdot10^{-3}$
Cd	2833,02	5,4	Tl 2580,14	4,8	$1\cdot10^{-5}-1\cdot10^{-3}$
Sb	2598,53	6,0	Tl 2580,14	4,8	$1\cdot10^{-4}-3\cdot10^{-3}$

The sensitivity of the method is $1 \times 10^{-5}\%$ for Bi and Cd; $3 \times 10^{-5}\%$ for Pb and Sn; and $1 \times 10^{-4}\%$ for Sb.

The reproducibility of the method, which is characterized by the mean square error, is 8% for Bi; 10% for Pb and Sb; and 11% for Cd and Sn.

SUMMARY

A method is described for determining Bi, Cd, Sn, Pb, and Sb present as impurities ($1 \times 10^{-4}\%$) in tantalum; an evaporation technique is used after conversion of the tantalum into its pentoxide.

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THE MASS-SPECTROMETRIC ANALYSIS OF THE ISOTOPIC COMPOSITION OF BORON

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The most widely used method for the determination of the isotopic composition of boron is the mass-spectrometric method in which boron trifluoride is used as the working material. During a study of the isotopic composition of boron in its oxide and acid, it is best not to convert the latter into BF_3, but to subject it directly to mass-spectrometric analysis. Shyuttse [1] studied the isotopic composition of boron in boron oxide, using an ionic source with a platinum crucible-evaporator and using B^+ ions; the accuracy was considerably lower than when BF_3 and BCl_3 are used, since it was not possible to get the required constancy for the source of the ionic currents. Inghram et al [2], while studying the mass spectrum of the vapors over liquid B_2O_3, detected $B_2O_3^+$, $B_2O_2^+$, BO^+ in the proportions 20 : 3.7 : 2.2 : 1.

Our measurements were made on the MS-1 and MS-4 mass spectrometers by the single-beam method. We were compelled to leave out the ionic source with the evaporating block which forms part of the MS-4 mass spectrometer, in view of the excessively large power used by the spiral of the source, which makes it difficult to control the current of the residual gases during the operation. We chose instead another ionic source, which in details of construction did not differ from that described earlier [3, 4] apart from the fact that the ribbon-evaporator was made from platinum on the surface of which was stamped out a cavity in the shape of a channel. The temperature of the ribbon was determined on the basis of the filament current, with preliminary calibration by means of an optical pyrometer. The optimum operating temperature of the evaporator was 1000-1200°.

About 0.5 mg of fused boron oxide was placed on the evaporator. This amount was sufficient for continuous work over a period of 3-4 hours, during which the stability of the ionic currents was completely satisfactory.

The following ions were observed in the mass spectrum of the vapors over boron oxide: $B_2O_3^+$, $B_2O_2^+$, BO^+ B^+ in the proportions of 19 : 3.1 : 2.2 : 1, which are in good agreement with published results [2]. Ions containing more than two atoms of boron were not detected. The isotopic composition of boron was determined using the ions $B_2O_3^+$ and B^+. Results of the study of B_2O_3 with a natural content of boron isotopes are given in Table 1.

The isotopic composition of boron in B_2O_3 was also determined by converting the latter into phenyldiazonium fluoroborate [5] with subsequent thermal decomposition of this material. The BF_3 liberated was analyzed on the mass spectrometer. These results are also given in Table 1. No corrections were applied for the content of the heavy isotopes of oxygen in making the calculations.

As is evident from Table 1, the results obtained during the measurements of the isotopic composition of boron on two different apparatus and at different times, are reproducible with reasonable accuracy.

Using the method developed, we determined the isotopic composition of boron for several samples of boron oxide with variable isotopic composition. Results of these experiments are given in Table 2. Here, as in the case of boron oxide B_2O_3 with a natural ratio of boron isotopes, we carried out a comparative determination, by converting the oxide into BF_3.

For removing the residues of test material completely, it is sufficient to wash the anode box, the ribbon-evaporator and holder, focussing block, and extension lens in alcohol.

TABLE 1

Isotopic Composition of Boron in B_2O_3 Without Enrichment with the B^{10} Isotope

Date on which meas. was made	Apparatus	Test material	Ion	Mean of 15-20 measurements
06.VIII. 1957	MS-4	B_2O_3	$B_2O_3^+$	4,16±0,05
08.VIII. 1957	MS-4	B_2O_3	$B_2O_3^+$	4,18±0,04
12.VIII. 1957	MS-4	B_2O_3	$B_2O_3^+$	4,15±0,04
14.VIII. 1957	MS-1	B_2O_3	$B_2O_3^+$	4,15±0,01
16.VII. 1957	MS-1	B_2O_3	$B_2O_3^+$	4,15±0,02
28.X. 1957	MS-4	B_2O_3	$B_2O_3^+$	4,16±0,04
29.X. 1957	MS-4	B_2O_3	$B_2O_3^+$	4,16±0,03
30.X. 1957	MS-4	B_2O_3	$B_2O_3^+$	4,17±0,03
			B^+	4,20±0,03
			$B_2O_3^+$	4,17±0,03
21.XI. 1957	MS-4	B_2O_3	B^+	4,18±0,01
			BF^+	4,20±0,04
30.XI. 1957	MS-1	BF_3	B^+	4,22±0,05

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*Mean of 15-20 measurements.

Shyuttse [1] during the evaporation of B_2O_3 observed in two of the thirty experiments a change in the ratio of B^{11}/B^{10} with time; this is contrary to what might be expected: at the beginning of the test there was observed preferential evaporation of molecules containing the heavy isotope B^{11}. The author does not give any theoretical foundation for this phenomenon. In our experiments the evaporation process took a comparatively short time, but orientating results indicated a normal process of isotope fractionation. All the same, insufficient experimental data do not give us the right at the moment to make any definite conclusion with regard to this effect.

TABLE 2

The Isotopic Composition of Boron in B_2O_3 Enriched with the B^{10} Isotopic

Sample No.	Test material	Ion	B^{11}/B^{10}	Sample No.	Test material	Ion	B^{11}/B^{10}
1	B_2O_3	B^+	0,100±0,001	2	B_2O_3	B^+	0,112±0,003
		$B_2O_3^+$	0,098±0,002	3	B_2O_3	B^+	0,147±0,001
1	B_2O_3	B^+	0,100±0,001			$B_2O_3^+$	0,145±0,003
		$B_2O_3^+$	0,097±0,001	1	BF_3	B^+	0,103±0,003
2	B_2O_3	B^+	0,108∓0,003				

Taking into account the simplicity of the method suggested, and also the reasonable reproducibility and accuracy of the results, it can be recommended for the isotopic analysis of boron.

SUMMARY

A method of evaporation from a ribbon is used for the mass-spectrometric isotopic determination of boron in boron oxide and boric acid.

The isotopic composition of boron in boron oxide with natural and altered ratios of the isotopes has been measured.

The analytical results were checked by carrying out measurements with BF_3 as the working substance.

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DETERMINATION OF THE VARIOUS FORMS OF IRON IN ROCKS

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Methods of determining iron in rocks have been extensively developed, and have been described in a number of textbooks [1-4]. Nevertheless, when we had to determine separately the various forms of iron in rocks (mainly in hydrothermally modified quartz porphyry), we were unable to find a published method which is rapid and fairly accurate. In the samples we had at our disposal, the iron(di-and trivalent-)was present partly in the form of oxides, partly combined as silicates, and also in the form of pyrites.

We adopted the following technique for determining di- and trivalent iron and iron combined in the form of pyrites, on one aliquot. 1 g (or 0.5 g) of rock which is not too finely ground is decomposed in a stream of CO_2 with a mixture of about 20 ml of dilute (1 : 2) sulfuric and about 10 ml hydrofluoric acid, in a special platinum test tube or crucible with an ebonite cover; through the latter a tube is passed which almost reaches the bottom. After cooling, the mixture is poured out into about 80 ml of a saturated boric acid solution and the ferrous iron determined by titration with 0.1 N potassium permanganate exactly according to the method described by Ponomarev [1], with the only difference that more boric acid is taken for complexing all the fluoride ions.

During the treatment described above, iron oxides and iron-containing silicates are decomposed, while the pyrites do not break down; grains of the latter are visible after titration under a magnifying glass. (For a discussion of the decomposition of pyrites when various methods are used for decomposing iron-containing materials, see Gillebrand et al [4], pp. 906 and 912).

Accordingly, after titration with permanganate, the solution is filtered through a loose filter and the precipitate washed with water until the washing give a negative reaction with thiocyanate (4-6 times) — a small amount of ammonium thiocyanate solution is placed in the funnel stem from which the wash liquors drop. To the filtrate, about 15 ml of 25% NH_4SCN is added, and the total amount of iron contained in the sample and now brought into solution by the acid treatment as ferric iron, titrated with 0.1 N $Hg_2(NO_3)_2$ as described by Ponomarev [2]. The amount of Fe^{III} is calculated by difference.

The filter paper plus pyrites is ignited and calcined at about 800° in a platinum or quartz crucible; the ferric oxide formed is fused with potassium pyrosulfate. The melt is dissolved on heating in dilute (1 : 20) H_2SO_4. A clear solution is obtained; occasionally a small crystalline precipitate is observed on the bottom of the beaker; this is, usually, insoluble sulfates. The solution is cooled (under the tap) and the iron originally contained in the pyrites, and now in the form of Fe^{III} of solution, determined by titration with $Hg_2(NO_3)_2$.

The method is applicable to the analysis of materials not containing appreciable (in comparison with the iron content) amounts of oxidizing-reducing agents, i.e., to the analysis of most of the common rocks. The deviation between parallel determinations does not exceed more than some hundredths of a percent (absolute). The method gives good results for some tenths of a percent, and upwards, of iron in rocks.

Using this method, up to five determinations can be carried out in a working day, when one platinum test tube is available for decomposing the sample.

The basic virtue of the method is the possibility of carrying out a rapid and accurate determination of the various forms of iron on one aliquot; this excludes the error connected with the heterogeneity of the sample (especially since it is recommended that the sample should not be ground too fine so as to avoid oxidation); the method also permits determination when only a small amount of material is available.

The author wishes to thank P. N. Palei for valuable advice and help, and A. I. Ponomarev for acting as a consultant on the use of the mercurimetric method.

SUMMARY

A method is described for the determination of di- and trivalent iron, and iron pyrite on one aliquot.

Fe^{II} is determined by a permanganate titration after decomposition of the rock with HF and H_2SO_4. Pyrite is not decomposed by the acids and is filtered off; $Fe^{II} + Fe^{III}$ is then determined in the filtrate by means of $Hg_2(NO_3)_2$ titration. The pyrite is ignited and fused with $K_2S_2O_7$, and the iron titrated with $Hg_2(NO_3)_2$ after dissolving the melt.

The method can be used for the analysis of material not containing appreciable (in comparison with the iron content) amounts of oxidizing-reducing agents; i. e., it can be used for most of the usual rocks. The deviation between parallel determinations does not exceed some hundredths of a percent (absolute). The method permits determination of several tenths of a percent and upwards of iron in rocks.

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A MICRO METHOD FOR THE DETERMINATION OF FLUORINE MONOXIDE

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Fluorine monoxide F_2O is a colorless, extremely poisonous gas which is even more dangerous than elemental fluorine [1]. This makes it essential to carry out systematic control of the air in places where fluorine monoxide is used.

When present in high concentrations F_2O is determined iodometrically [2]; $OF_2 + 4KI + H_2O \rightarrow 2I_2 + 2KOH + 2KF$.

The aim of the work described here was to develop a method for determining gamma amounts of F_2O in air. Basing our efforts on the properties of F_2O as a strong oxidizing agent, we tried to use analytical reactions of the oxidation-reduction type which are accompanied by the formation of a color directly in the absorptive solution. All the same, many experiments made along these lines did not yield satisfactory results. Fluorine monoxide, in contrast to elemental fluorine, reacts extremely slowly with aqueous solutions of reagents, which is explained, presumably, by its low solubility in water.

The essence of the method which we have developed for determination of traces of fluorine monoxide in air reduces to liberation of bromine from potassium bromide and formation of tetrabromofluorescein (eosin) which is colored red. On drawing air containing F_2O through indicator powder on a silica gel base, the initial yellow color of the indicator changes to red; the length of the colored zone being proportional to the amount of fluorine monoxide. In the course of numerous experiments in which known amounts of F_2O were used, the optimum conditions for determining the latter were established, and a conversion factor determined experimentally. Under the conditions we used, 1 mm of the colored zone was equivalent to 0.334 γ F_2O.

Below is given the method for preparing the indicator tubes and the experimental procedure.

Glass tubes 45 mm long and with an internal diameter of 2.5 mm are filled with indicator powder.* A cotton wool plug is fitted into one of the glass tubes, while into the other end, the open end, is poured the indicator powder through a funnel with a drawn-out end; the indicator powder consists of silica gel Msk, 260-300 μ, moistened with a solution of fluorescein containing KBr and K_2CO_3. By closing the upper end of the tube with the finger and lightly tapping the walls, the column of powder is packed, and sufficient powder introduced to give a column 40 mm long. The surface of the column is covered with a thin layer of cotton wool which is packed by squeezing it with the help of a fine metal rod. The ends of the tube are sealed with plugs and wrapped up in black paper for storage.

It is essential to standardize the conditions for preparing the indicator tubes, since the diameter of the tube, the packing density, the size of the silica gel particles, and the concentration of the reagents in the solution used for moistening the powder, all affect the length of the colored zone.

The fluorine monoxide content of the air to be tested is determined as follows: the plugs are removed from one of the tubes and one end connected to a 1 liter capacity aspirator; 1 liter of air is then drawn through at an uniform rate in the course of 20 minutes. The indicator tube is disconnected and the length of the red colored zone measured with a millimeter ruler. The fluorine monoxide concentration of the air is determined in γ/liter, using the coefficient 0.334.

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*The method of preparing the indicator powder has been described in the article by Peregud and Boikina [3].

SUMMARY

A method for the determination of fluorine monoxide is based on liberation of bromine from potassium bromide and the subsequent formation of eosin. When air containing F_2O is drawn through the indicator tube containing silica gel and fluorescein, the original color turns red. The length of the colored zone is proportional to the quantity of fluorine monoxide. Optimum conditions for determining F_2O have been established.

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DETERMINATION OF THALLIUM BY HIGH-FREQUENCY TITRATION WITH SODIUM TETRAPHENYLBORON

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The solubility of thallium tetraphenylboron is 5-6 γ in 100 ml at 20° according to Geilmann[1]. We have studied the possibility of carrying out high-frequency titration (H. F. T.) of thallium with sodium tetraphenylboron:

$$Tl_2SO_4 + 2Na[B(C_6H_5)_4] = 2Tl[B(C_6H_5)_4] + Na_2SO_4.$$

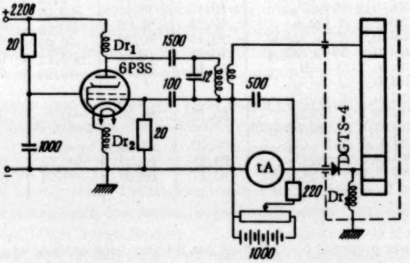

Fig. 1. Schematic diagram of the apparatus used for high-frequency titration.

Sander and Anke [2] have used sodium tetraphenylboron for the conductometric determination of potassium and ammonium. The advantages of H. F. T. have been pointed out in the work of Zarinskii and Mandel'berg [3].

Apparatus and experimental procedure. The setup used for the work was a modified form of the Blake apparatus [4] suggested by Resnais [5]; in this apparatus the strength of the high-frequency current passing through the titration cell is measured (Fig. 1).

The frequency of the high-frequency current used was about 14 megacycles; this permits work in solution down to 0.25 M concentration. A condenser-type cell with a capacity of 25-30 ml was used for titration. The high-frequency current passing through the cell was rectified with a germanium diode and was measured with a milliammeter.

The reagent was added from a semimicro buret and was read to an accuracy of ± 0.005 ml.

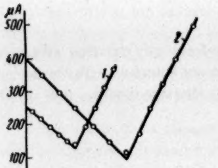

Fig. 2. Titration curves of thallium sulfate. 1) 1 ml of 0.1 N thallium sulfate; 2) 2ml of 0.1 N thallium sulfate.

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*Translated from the Russian.

The solution was agitated by means of a mechanical stirrer. The test solution of thallium sulfate was measured out with a pipet (or semimicro buret) and was diluted in the titration cell to 25 ml with water. The equivalence point was determined graphically by plotting the amount of solution added in ml, along the abscissa, and the value of the high-frequency current, along the ordinate; when $R_{galvanometer} = 150$ Ω, 100 divisions on the milliammeter corresponded to 0.5 ma. A titration curve is shown in Fig. 2. The lower the value of $R_{galvanometer}$ for a given sensitivity of the galvanometer, the higher the sensitivity of the apparatus at higher concentrations of the electrolyte.

Sodium tetraphenylboron was synthesized according to [6]. A 0.2 M solution was used; in order to remove insoluble impurities from the latter, 2 g of hydrated alumina was added per 100 ml of solution (bemite modification). The solution was agitated for one hour and then filtered. A solution prepared in this way and stored in a well sealed vessel, kept its titer for several months. It was standardized by H. F. T. against 0.1 N KCl.

Titration of Thallium with Sodium Tetraphenylboron

0,1 N Tl_2SO_4, ml	Impurity	Tl found, mg	Tl taken, mg	Error	
				in mg	in %
0,5	—	5,15	5,10	+0,05	0,98
1,0	—	10,28	10,20	+0,08	0,78
2,0	—	20,34	20,40	—0,0	0,25
1,0	2 ml 0,1 N NaCl	10,12	10,20	—0,08	0,78
1,0	5 ml 0,1 N NaCl	10,17	10,20	—0,0	0,29
1,0	2 ml 0,1 N $ZnSO_4$	10,16	10,20	—0,04	0,39
1,0	5 ml 0,1 N $ZnSO_4$	10,12	10,20	—0,08	0,78
1,0	2 ml 0,1 N $CdCl_2$	10,19	10,20	—0,01	0,09
1,0	5 ml 0,1 N $CdCl_2$	10,19	10,20	—0,01	0,09
1,0	2 ml 0,1 N $Cu(NO_3)_2$	10,13	10,20	—0,07	0,68
1,0	5 ml 0,1 N $Cu(NO_3)_2$	10,21	10,20	+0,01	0,09
1,0	2 ml 0,1 N $CdCl_2$ 2 ml 0,1 N $CuCl_2$	10,16	10,20	—0,04	0,39
1,0	4 ml 0,1 N $ZnSO_4$ 4 ml 0,1 N $CdCl_2$ 2 ml 0,1 N $Cu(NO_3)_2$	10,19	10,20	—0,01	0,09
1,0	2 ml 0,1 N Na_2CO_3	10,20	10,20	—	—
1,0	2 ml 0,1 N H_2SO_4	10,22	10,20	+0,02	0,18
1,0	5 ml 0,1 N CH_3COOH	10,19	10,20	—0,01	0,09

0.1 N thallium sulfate was prepared by weighing out the requisite amount of anhydrous Tl_2SO_4 (chemically pure grade).

The titration results obtained are given in the Table. As these results show, the presence of sodium, zinc, cadmium, and copper salts in solution does not interfere with the thallium deterimination.

SUMMARY

A new method has been developed for the determination of thallium by high-frequency titration with sodium tetraphenylboron. Salts which do not react with sodium tetraphenylboron do not interfere with the determination of thallium. Thallium can be determined both in weakly acid and in alkaline media.

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A COMPARATIVE STUDY OF THE SPATIAL DISTRIBUTION OF ELEMENTS IN A D.C. ARC AND IN AN IMPULSE ARC BY MEANS OF RADIOACTIVE ISOTOPES

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It was demonstrated recently [1] that the use of an impulse arc operating according to the scheme suggested by Levintov [2], makes it possible to increase the accuracy and reproducibility of the spectrographic analysis of silicates appreciably. In the course of this work a number of factors were observed which can be interpreted as indicating a distribution of the elements in the interelectrode space which differs essentially from the one observed in the normal d.c. arc. In order to study this observation experimentally, use was made of a method suggested in our laboratory [3] for studying the spatial distribution of elements in the plasma of various sources by means of radioactive isotopes. Radioactive isotopes have also been used [4,5] for studying the process of evaporation of various elements in an impulse arc and in a d.c. arc.

The experimental technique used has been described in the papers cited [3, 4]. The curves (Figs. 1 and 2) give an idea of the nature of the distribution of a number of elements in the interelectrode gap of a d.c. arc, and of an impulse arc. As is evident from the diagrams independently of the shape of the distribution curves of the elements in the plasma of the d.c. arc, for the majority of the elements in the impulse arc, there is observed an uniform distribution with a clearly defined maximum located in the middle of the interelectrode gap. The only exceptions are tha alkali metals with low ionization potential values. The spatial distribution of these elements in the different souces differs insignificantly. It should be pointed out that the curves for the spatial distribution of potassium* during its evaporation in both souces, from carbonate and sulfate, differ from each other. In the latter instance, in the middle region of the interelectrode gap there is observed a clearly defined minium, the incidence of which, presumably, is the reason for the weakening ofthe lines of a number of the alkaline metals on addition of relatively large amounts of sodium sulfate to the test material, a phenomenon which has been noted previously in the literature [6,7]. The levelling of the distribution curve for the atoms of the alkali elements in the plasma of an impulse arc, is favored by dilution of the salts of these elements by a buffer mixture consisting of carbon powder and cupric oxide. Thus, in the mixture consisting of these components in the proportion of 1:1:2, the distribution curve for sodium in an impulse arc acquires the shape shown in Fig. 3. In this case, as is evident, the character of the distribution of the alkali elements in the interelectrode, is already almost indistinguishable from the distribution characteristic for such elements as zinc and copper.

In order to get a clearer picture of the character of the distribution of elements in an impulse arc, and in order to compare this source with other sources, and also to get experimental data which would enable one to explain the mechanism of the passage of atoms of elements into the interelectrode space in this source, a detailed study was made of the spatial distribution of copper during its evaporation as metal in a spark, in a d.c. arc, and in an impulse arc. The photographs obtained of the arc in γ-radiation were photometrically measured in a large number of sections along and across the interelectrode gap; the results of the photometric measurements are represented in the form of isolines which delineate the plasma regions with equal (within the limits of the range chose for the blackening of the photographic plates) densities of the material. The results obtained are reproduced in Fig. 4. As is evident, in contrast to the spark source and the d.c. arc, in the plasma of which there is observed a sharp heterogeneous distribution of the material passing from the anode, and a scattering of this material toward the side in the spark, such heterogeneity is almost completely absent in the central zone of the interelectrode gap of an impulse arc. The second distinguishing feature of the diagram representing the spatial distribution of elements in the plasma of this source, is the presence in it of a characteristic "protuberance", characterized by enhanced density, and directly related to the material located in the anode crater. It might be thought that in this way there is a periodic "injection" of the molten mass of the test element * into the interelectrode gap of the source. If this assumption were to be confirmed by further and more detailed experimental work, it would clarify a number of the characteristics of the source described, attention to which has been drawn in a previous paper [1], and would open up a way of solving the question of the use of melts in the practice of spectrographic analytical work.

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*Similar phenomena have also been observed for sodium salts.

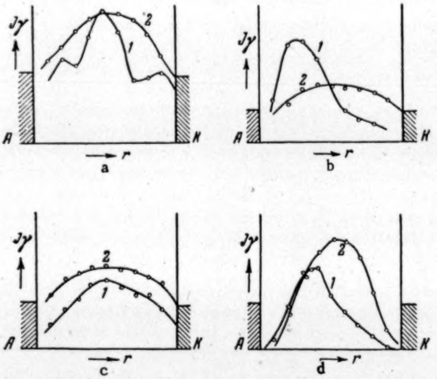

Fig. 1. Distribution of gallium (a), zinc (b), iron (c), and copper (d) in the interelectrode gap of a d.c. arc (1) and impulse arc (2), during evaporation of the elements from their oxides. Labelled atoms Ga^{72}, Fe^{55}, Zn^{65} and Cu^{64}.

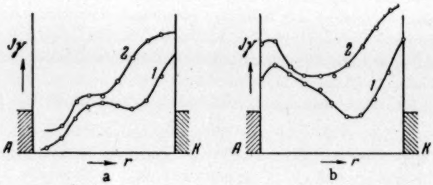

Fig. 2. Distribution of potassium in the interelectrode space of a d.c. arc (1) and an impulse arc (2) during evaporation of the element in the form of K_2CO_3 (a) and K_2SO_4(b). Labelled atom K^{42}

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*This mechanism of the passage of elements into the plasma of the source may be occur alongside the usual fractional evaporation.

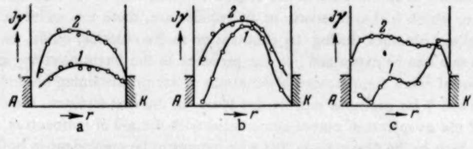


Fig. 3. Distribution of zinc (a), copper (b), and sodium (c) in the interelectrode space of an impulse arc during their evaporation from pure ZnO, CuO, and Na_2CO_3 (1) and from their mixture (2) with graphite and cupric oxide in the proportion 1:1:2.

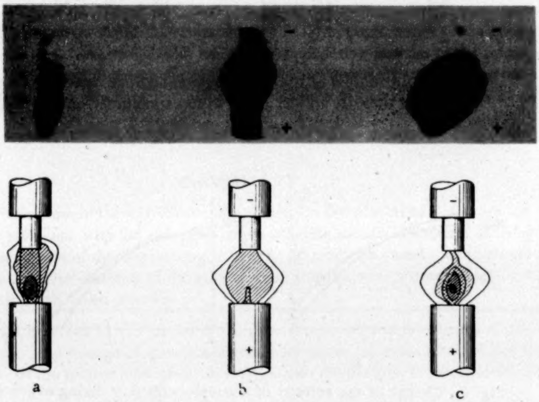
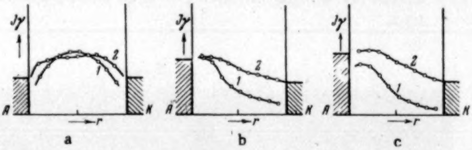


Fig. 4. Photographs of the interelectrode space of a spark (a), an impulse arc (b), and a d.c. arc (c), taken in γ-radiation from Cu^{64}, and the corresponding diagrams representing the distribution of the elements in the plasma of the sources.

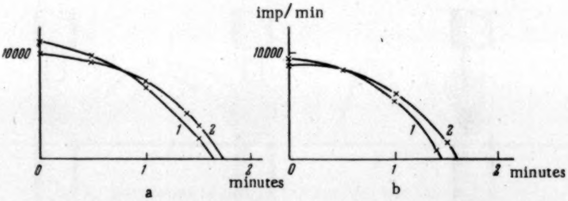
The first interesting results which we were able to obtain by using radioactive isotopes for studying the kinetics of the evaporation and distribution of elements in the plasma of various sources, were those obtained on evaporating AgCl. As shown earlier [3], the spatial distribution curves obtained for silver in the interelecttrode space of a d.c. arc during the evaporation of this elements as its chloride, oxide, and as the metal itself differ essentially from each other. This testifies to differences in the statein which the test element passes into the arc plasma in the first and in the other two cases, and may be interpreted as indicating that the atoms of silver are not found as simple ions in the plasma.

This question was subjected to additional, and more systematic study, in the work described here. A comparison was made of the curves characterizing the distribution of silver in the interelectrode gap of a d.c. arc and an impulse arc, during the evaporation of this element as the chloride, oxide, and metal (Fig. 5); curves were also obtained for the changes in the activity of the samples with time during evaporation of AgCl with radioactive isotopes of Ag and Cl in both sources (Fig. 6). For comparison, the evaporation curves of Na and S, entering into the composition of sodium sulfate (Fig. 7), were also studied in the same sources by means of radioactive isotopes. The experimental results obtained completely confirm previous observations and show that, despite the tendency to an increase in the degree of uniformity of the distribution of the elements in the interelectrode space, which is characteristic of an impulse arc, there are, nevertheless, differences in the distribution curves for silver obtained during its evaporation as the chloride, oxide, or metal in this source also. It is very likely that this can be explained , by the presence in the interelectrode space, not of the simplest ions or atoms of silver, but of more complicated associations of atoms containing chlorine atoms. A comparison of the curves in Figs. 6 and 7 for example support this idea. In the first instance, they testify to the almost complete coincidence of the evaporation curves constructed with the aid of radioactive atoms of silver and chlorine, the time of stay of which in the plasma, in this way, proves to be coincident in both sources. In contrast to this, the curves for the change of activity with time for samples containing Na_2SO_4 (Fig. 7), into whose composition radioactive sodium or sulfur enter, differ sharply from each other even on complete dissociation of the salt.



a b c

Fig. 5. Distribution of silver in the interelectrode space of a d.c. arc (1) and an impulse arc (2) during evaporation in the form of AgCl(a),



a b

Fig. 6. Change in the activity of a sample with time during evaporation of AgCl with labelled atoms Ag^{110} and Cl^{36} in a d.c. arc (a) and impulse arc (b):

1) Measurements based on Cl; 2) measurements based on Ag.

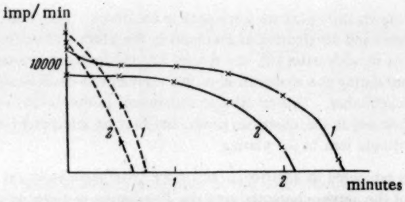


Fig. 7. Change in the activity of a sample with time during evaporation of Na_2SO_4 containing labelled isotopes Na^{24} and S^{35} in a d.c. arc (1) and an impulse arc (2):

Full line for $Na_2^{\bullet}SO_4$; dotted line for $Na_2S^{\bullet}O_4$

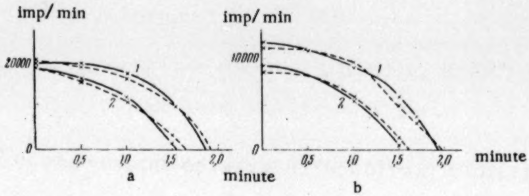


Fig. 8. Change in the activity of a sample with time during the evaporation of NaCl (a) and $CuCl_2$ containing radioactive Na^{24}, Cl^{36}, and Cu^{64} in a d.c. arc (1) and an impulse arc (2): Full line-measurements based on Cl; dotted lines-measurements based on Na and Cu respectively.

As is evident from a consideration of the results shown in Fig. 8, coincidence of the curves for change of activity of the sample with time, constructed with the help of radioactive isotopes of the metal and chlorine, is observed not only for AgCl, but also during the evaporation of the elements entering into the composition of other chlorides. The authors wish to thank N. P. Yakovlev for his help in carrying out the work described here.

SUMMARY

Independently of the nature of the distribution of elements in the plasma of a d.c. arc, in the impulse arc there is observed for all elements, with the exception of the alkaline metals, a uniform distribution with a maximum located in the middle of the interelectrode space. In order to smoothe out the curves for the distribution of atoms of the alkaline elements in the plasma of an impulse arc, it is necessary to dilute samples or salts of these elements with a buffer mixture.

Experimental results obtained for the spatial distribution of elements in the plasma of an impulse arc make it possible to postulate that, the passage of the elements into the interelectrode space of this source is realized by periodic "injections" of the molten mass of test material into the plasma, in addition to the usual fractional evaporation.

A study of the kinetics of evaporation and spatial distribution of elements in the plasma of an impulse arc and of a d.c. arc, taking various compounds of silver, and also the chlorides of silver and copper as test materials, has shown that there is a relationship between the corresponding curves and the type of compound used. This indicates that the atoms of these elements exist in different forms in the source plasma when they are evaporated in the form of different compounds.

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COMPLEXOMETRIC TITRATION WITH METALLO-INDICATORS

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Complexometric titration is widely used in modern analytical chemistry [1]. The properties of the most important complexons and of the complexes which these complexons give with various metal ions have been studied in fair detail [2-4]. The properties of such metallo-indicators as murexide and eriochrome black(chromogen black ET-00) have been studied less fully [5-7], while the study of certain new metallo-indicators has been confined simply to determining their sensitivity to various metal ions [8].

As for the general theory of the analytical application of complexons, the basic precepts advanced by Yatsimirskii [9] have not as yet received any further development, and in this connection therefore, there are so far, no correct ideas regarding the factors which affect the accuracy of certain determinations, and the possibility of successive titration in systems containing different metal ions, or regarding calculations which will ensure a critical choice of new procedures, and a rational self-critical conductance of complexometric determination.

The question of the determination of indicator errors reduces either to an evaluation of the equilibrium concentrations of all colored particles, for equimolar initial concentrations of the ions of the metal and the complexon, or to a calculation of the initial concentration of the complexon which will guarantee a given color intensity. For this purpose it is necessary to use the instability constants of the complexes formed with the metallo-indicator corresponding to a given pH of the system, and also to take into account the possible hydrolysis of all the interacting particles.

Let us take as an example the determination of Ca^{2+} by Schwarzenbach's method [1, p. 55], according to which, at a pH of 12.5 the following concentrations, (c) in moles per liter, hold good: $c_{Ca^{2+}} = 10^{-2}$, $c_{NH_4H_4\pi} = c_{NH_4^+} = c_{H_4\pi^-} = 3.3 \cdot 10^{-5}$ ($NH_4H_4\pi$ -is ammonium purpurate). As a start we shall try to explain what will be the intensity of the color of the system after addition of $c_{Na_2H_2R} = c_{H_2R^{2-}} = 10^{-2}$ (Na_2H_2R is Complexon III). Preliminary calculations * show that at a pH of 12.5, about 39 % of Ca is found in the form of $CaOH^+$ ions, 99.4% of Complexon III in the form of R^{4-} ions, and approximately 97% of murexide in the form of $H_2\pi^{3-}$ ions.

The following equilibria occur in solution:

$$Ca^{2+} + H_2O \rightleftarrows CaOH^+ + H^+ \quad pK_1 = 12{,}7 \tag{1}$$

$$CaH_2\pi^- \rightleftarrows Ca^{2+} + H_2\pi^{3-} \quad pK_2 = 5{,}1 \tag{2}$$

$$CaR^{2-} \rightleftarrows Ca^{2+} + R^{4-} \quad pK = 9{,}2 \text{ for } \mu = 0{,}7. \tag{3}$$

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*For these calculations the following values were used: pK - 12.7 for hydrolysis of Ca^{2+} ions [10], pK_3 = 6.16 and pK_4 = 10.26 for the dissociation of ethylenediaminetetracetic acid [11], and pK_2 = 9.2 and pK_3 = 10.9 for purpuric acid [12].

Let us designate $[H^+] = 10^{-12.5}$ by h, and $c_{H_2\pi 3} = 3.3 \cdot 10^{-5}$ by c_1.

$$c_{Ca^{2+}}' = c_{R^{4-}} = 10^{-2} = c,\ [CaOH^+] = x,\ [Ca^{2+}] = y,\ [CaH_2\pi^-] = z,$$

$$[CaR^{2-}] = u,\ [H_2\pi^{3-}] = v,\ [R^{4-}] = t.$$

Using the usual methods for calculating equilibrium [13], we obtain the system of equations

$$hx = K_1 y \quad (4) \qquad c = x + y + z + u \quad (7)$$

$$yv = K_2 z \quad (5) \qquad c = u + t \quad (8)$$

$$yt = Ku \quad (6) \qquad c_1 = z + v \quad (9)$$

which readily reduce to the equation

$$\begin{gathered}(h + K_1)\, y^3 + [c_1 h + (h + K_1)(K + K_2)]\, y^2 - \\ - K\, [h(c - c_1) - K_2 (h + K_1)]\, y - chKK_2 = 0\end{gathered} \tag{10}$$

After substituting the values of known factors and transforming we get the cubic equation

$$y^3 + 2{,}820 \cdot 10^{-5} y^2 - 3{,}851 \cdot 10^{-12} y - 3{,}073 \cdot 10^{-17} = 0,$$

which is readily solved by Horner's method [13]. As a result we find that $y = [Ca^{2+}] = 1.1 \cdot 10^{-6}$, $x = [CaOH^+] = 6.9 \cdot 10^{-7}$, $z = [CaH_2\pi^-] = 4.0 \times 10^{-6}$, $v = [H_2\pi 3^-] = 2.9 \cdot 10^{-5}$, $u = [CaR^{2-}] = 9.992 \cdot 10^{-3}$ and $t = [R^4] = 5.8 \cdot 10^{-6}$.

The color of the solution is determined by the ratio $v{:}z = [H_2\pi 3^-] : [CaH_2\pi^-] = 7.3$. Since the concentration of the blue ions of $H_2\pi 3^-$ is 7.3 times the concentration of the red ions of $CaH_2\pi^-$, the color of the mixture should be a blue-violet as indicated in Schwarzenbach's procedure.

It must be specially emphasized that $pK_2 = 5.1$ for the instability of $CaH_2\pi^-$, is taken from the special table of Schwarzenbach for a pH of 12.5.

We shall now carry out a similar calculation for the determination of Mg^{2+} ions using eriochrome black-T(NaH_2E) as indicator [1, p. 56]. Transforming the concentrations into moles per liter leads to the values: $c_{Mg^{2+}} = 8 \cdot 10^{-3}$ and $c_{NaH_2E} = 2.5 \cdot 10^{-5}$ (at pH 10). Preliminary calculations lead to the following: at a pH of 10, more than 16% of the Mg is found in the form of $MgOH^+$ ions; 97.3% of the indicator is in the form of NE^{2-} ions, while Complexon III gives 64.5% of HR^{3-} ions and 35.4% of R^{4-} ions.*

On this basis, the initial conditions of the problem, after addition of an equivalent amount of Complexon III, are determined by the following data: pH 10, $c_{Mg^{2+}} = 8 \cdot 10^{-3} = c$, $c_{HE^{2-}} = 2.5 \cdot 10^{-5} = c_1$ and $c_{HR^{3-}} = 8 \cdot 10^{-3} = c$. We get the following equilibria:

$$Mg^{2+} + H_2O \rightleftarrows MgOH^+ + H^+ \quad pK_1 = 10{,}7 \tag{11}$$

$$HE^{2-} \rightleftarrows H^+ + E^{3-} \quad pK_{13} = 11{,}52 \tag{12}$$

$$HR^{3-} \rightleftarrows H^+ + R^{4-} \quad pK_{24} = 10{,}26 \tag{13}$$

$$MgR^{2-} \rightleftarrows Mg^{2+} + R^{4-} \quad pK = 8{,}69 \tag{14}$$

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*The following values were used in these calculations: pK = 11.7 for the hydrolysis of Mg^{2+} ions [10, p. 314] and $pK_2 = 6.3$ and $pK_3 = 11.52$ for eriochrome black T [7].

$$\mathrm{MgE}^- \rightleftarrows \mathrm{Mg}^{2+} + \mathrm{E}^{3-} \quad pK_2 = 5 \tag{15}$$

the value of pK_2 is taken from Schwarzenbach's graph at a pH of 10 [5].

The following designations are used $[\mathrm{Mg}^{2+}] = x$, $[\mathrm{MgOH}^+] = y$, $[\mathrm{HE}^{2-}] = z$, $[\mathrm{E}^{3-}] = u$, $[\mathrm{HR}^{3-}] = v$, $[\mathrm{R}^{4-}] = w$, $[\mathrm{MgR}^{2-}] = t$, $[\mathrm{MgE}^-] = s$; then proceeding according to the general rules [13] we obtain the following system or equations

$$hy = K_1 x \quad (16) \qquad xu = K_2 s \quad (20)$$

$$hu = K_{13} z \quad (17) \qquad c = x + y + t + s \quad (21)$$

$$hw = K_{24} v \quad (18) \qquad c = v + w + t \quad (22)$$

$$xw = Kt \quad (19) \qquad c_1 = z + u + s, \quad (23)$$

which reduce to the equation

$$hK_{13}As^3 + \{hK_{13}[D - (c_1A - B) - cA] - AE\}\,s^2 - \\ - \{BE + hK_{13}[c_1(B + D) - c(c_1A - B)]\,s + cc_1hK_{13}B\} = 0 \tag{24}$$

where

$$A = K_2K_{24}(h + K_{13}) - KK_{13}(h + K_{24}),$$
$$B = c_1KK_{13}(h + K_{24}),$$
$$D = cK_2K_{24}(h + K_{13}),$$
$$E = K_2(h + K_1)(h + K_{13}).$$

After substituting the values of h, c_i, and K_i, and carrying out the usual transformations we get the equation

$$s^3 - 4{,}683\cdot 10^{-4}s^2 - 1{,}868\cdot 10^{-13}s + 8{,}441\cdot 10^{-17} = 0 \tag{25}$$

The first positive root of this equation $s_1 = [\mathrm{MgE}^-] = 4.683 \cdot 10^{-4}$ does not satisfy the initial conditions of the problem, since the value of $t = [\mathrm{MgR}^{2-}] = 8 \cdot 10^{-3}$ and the sum $s_1 + t \approx 8.5 \cdot 10^{-3}$, calculated by means of it, are greater than $c_{\mathrm{Mg}^{2+}} = 8 \cdot 10^{-3}$. An approximate value of the second root $s_2 \sim 4.3 \cdot 10^{-7}$ can be found from the equation $s^2 = 1.868 \cdot 10^{-13}$, while an accurate value can be found by the method of successive approximation. All the equilibrium concentrations are calculated by means of it: $s = [\mathrm{MgE}] = 4.245 \cdot 10^{-7}$, $u = [\mathrm{E}^{3-}]$

$$u = [\mathrm{E}^{3-}] = 7{,}2\cdot 10^{-7},\ z = [\mathrm{HE}^{2-}] = 2{,}4\cdot 10^{-5},\ x = [\mathrm{Mg}^{2+}] = 5{,}9\cdot 10^{-6},$$
$$y = [\mathrm{MgOH}^+] = 1{,}2\cdot 10^{-6},$$

The color of the equilibrium system is determined by the ratio between the concentrations of the blue HE^{2-} particles, the red MgE^- particles, and the orange E^{3-} ions. In our case

$$\frac{[\mathrm{HE}^{2-}]}{[\mathrm{MgE}^-] + [\mathrm{E}^{3-}]} = \frac{2{,}4\cdot 10^{-5}}{4{,}2\cdot 10^{-7} + 7{,}2\cdot 10^{-7}} = 21,$$

this indicates that the color of the solution after addition of an equivalent amount of Complexon III should be pure blue, as indicated in Schwarzenbach's procedure.

Since, however, a pure blue color should already be obtained at a ratio of $[HE^{2-}]$: $([MgE^-] + [E^{3-}]) = 10$, it is obvious that the procedure includes a systematic error. In order to evaluate this error it is necessary to calculate $c_{HR^{3-}}$ so that

$$[HE^{2-}] = 10\ [MgE^-] + [E^{3-}]) , \tag{26}$$

then the error will be equal to $c_{Mg^{2+}} - c_{HR^{3-}}$. In this case a new unknown appears $c_{HR^{3-}} = \varphi$ and, at the same time, the additional condition (26). Using the same designations as before for the unknown equilibrium concentrations we get a new system of equations which satisfy the equation

$$z = 10(u + s), \tag{27}$$

and instead of equation (22) contains the equation

$$\varphi = v + w + t. \tag{28}$$

The new system is solved much more easily than the previous one, and gives the following results: $z = [HE^{2-}] = 2.27 \cdot 10^{-5}$, $u = [E^{3-}] = 6.86 \cdot 10^{-7}$,

$$s = [MgE^-] = 1{,}59 \cdot 10^{-6},\ x = [Mg^{2+}] = 2{,}31 \cdot 10^{-5},\ y = [MgOH^+] = = 4{,}61 \cdot 10^{-6},$$

$$t = [MgR^{2-}] = 7{,}97 \cdot 10^{-3},\ w = [R^{4-}] = 7{,}04 \cdot 10^{-7},$$

$$v = [HR^{3-}] = 1{,}28 \cdot 10^{-6}$$

and, finally

$$c - \varphi = x + y + s - (v + w) = 2{,}7 \cdot 10^{-5}$$

from which the error sought is

$$\Delta = -\ 0.34\%$$

The problem of the successive titration of two metal ions B and M with concentrations $c_B = c_1$ and $c_M = c_2$ is solved by different methods depending on the pH at which the titration is carried out.

Let us assume that at the given pH, hydrolysis of the complexon can be disregarded. Since, (in such cases,) it is necessary to take into account hydrolysis of the metal ions, let us consider the following complex of equilibria

$$BR \rightleftarrows B + R \qquad K_{11} \tag{29}$$

$$B + H_2O \rightleftarrows BOH + H \qquad K_{12} \tag{30}$$

$$MR \rightleftarrows M + R \qquad K_{21} \tag{31}$$

$$M + H_2O \rightleftarrows MOH + H \qquad K_{22} \tag{32}$$

Let us assume that $K_{11} < K_{21}$. In this case it is ion B that will be titrated mainly, while if it is assumed that toward the completion of titration the initial concentration of the reagent $c_R = c_1$, then it can be assumed that $[BR] = (1 - \alpha)c_1$ and $[MR] = \alpha c_1$, where $0 < \alpha < 1$. The following are unkown $[B] = x$, $[BOH] = y$, $[BR] = z$, $[R] = u$, $[M] = v$, $[MOH] = w$, $[MR] = t$ and α. According to general rules we write the system of equations

$$xu = K_{11}z \quad (33) \qquad z = (1 - \alpha)c_1 \quad (37)$$

$$hy = K_{12}x \quad (34) \qquad t = \alpha c_1 \quad (38)$$

$$uv = K_{21}t \quad (35) \qquad c_1 = x + y + z \quad (39)$$

$$hw = K_{22}v \quad (36) \qquad c_2 = v + w + t \quad (40)$$

The solution

$$\alpha = \frac{(-q+1)+\sqrt{(q+1)^2+4q(Q-1)}}{2(Q-1)}, \qquad (41)$$

where,

$$q = c_2/c_1, \; Q = K_{21}(h+K_{22})/K_{11}(h+K_{12}), \qquad (42)$$

makes it possible to calculate the fraction of complexon α, combined with the second metal ion at the equivalence point. Thus, for the case of the successive titration of Ca^{2+} and Mg^{2+} ions at pH 12.5, pK$_{21}$ = 8.69, pK$_{22}$ = = 11.7, pK$_{11}$ = 10.59, and pK$_{12}$ = 12.7, and as a result

at q = 10	1	0.1
α = 0.160	0.066	0.054

i.e. even in the system where $c_{Mg^{2+}}$ = 0.1 $c_{Ca^{2+}}$, the titration error will be greater than 5%

At low pH values, similar calculations are complicated by the hydrolysis of the complexon, but are simplified somewhat by reduction of the hydrolysis of the metal ions.

Let us assume that in a system where $c_B = c_1$, $c_M = c_2$, $c_R = c_1$, and $K_{11} < K_{21}$, the following equilibria are established at a given pH

$$B + H_2O \rightleftarrows BOH + H \qquad K_{12} \qquad (43)$$
$$BR \rightleftarrows B + R \qquad K_{11} \qquad (44)$$
$$H_2R \rightleftarrows H + HR \qquad K_1$$
$$HR \rightleftarrows H + R \qquad K_2 \qquad (45)$$
$$MR \rightleftarrows M + R \qquad K_{21} \qquad (46)$$

(47)

Here the unkowns are [B] = x , [BOH] = y, [BR] = z, [R] = u, [H$_2$R] = v, [HR] = w, [MR] = t, [M] = s and α, and the following system of equations can be written

$$hy = K_{12}x \qquad (48) \qquad\qquad su = K_{21}t \qquad (52)$$
$$xu = K_{11}z \qquad (49) \qquad\qquad c_1 = x + y + z \qquad (53)$$
$$hw = K_1 v \qquad (50) \qquad\qquad c_2 = t + s \qquad (54)$$
$$hu = K_2 w \qquad (51) \qquad\qquad c_1 = z + u + v + w + t \qquad (55)$$
$$t = \alpha[c_1 - (u + v + w)] \qquad (56)$$

A solution of this system with respect to α is possible, but it leads to an equation of the third order

$$\begin{gathered} D[c_1hK_{21}(c_1+A)+c_2(c_1hK_{21}+AB)]\alpha^3 + \\ +\{hK_{21}(c_1hK_{21}+c_2B)(c_1+c_2) - D[c_1hK_{21}(c_1+A)+2c_2(c_1hK_{21}+AB)]\}\alpha^2 + \\ +c_2B[AD-2hK_{21}(c_1+c_2)]\alpha + c_2^2hBK_{21} = 0, \end{gathered}$$

where

$$A = K_2(h^2+K_1h+K_1K_2)/K_1K_2, \; B = K_{11}(h+K_{12}) \quad \text{and} \quad D = hK_{21}$$

For example, in the case of the procedure given by Yu. I. Usatenko and L I. Mikhailova [14] for the determination of Fe^{3+} by means of Complexon III at a pH of 1-2 in the presence of divalent metal cations, and using a specific indicator for Fe^{+}, pK$_{12}$ = 2.5 , pK$_{11}$ = 25.1, pK$_{21}$ = 10.59 (for Ca^{2+}), pK$_1$ = 6.16, pK$_2$ = 10.26, and h = 10^{-2}, if it is assumed that the pH is 2. For the case where c$_1$ = 10^{-2} and c$_2$ = 10, c$_1$ = 0.1,

$$\alpha^3 - 0{,}9997\,\alpha^2 + 4{,}072\cdot10^{-14}\,\alpha + 6{,}004\cdot10^{-17} = 0; \qquad (58)$$

of the two roots of equation (58): $\alpha_1 = 0.9997$ and $\alpha_2 = 7.8 \cdot 10^{-9}$, only the second one is suitable. As a result it follows that

$$z = [\mathrm{FeR}^-] \simeq c_1 = 10^{-2},\quad t = [\mathrm{CaR}^{2-}] = 7{,}8 \cdot 10^{-9},\quad s = [\mathrm{Ca}^{2+}] \simeq c_2 = 0{,}1,$$

$$u = [\mathrm{R}^{4-}] = 2 \cdot 10^{-20},\quad w = [\mathrm{HR}^{3-}] = 3{,}6 \cdot 10^{-12},\quad v = [\mathrm{H_2R}^{2-}] = 5{,}2 \cdot 10^{-8}.$$

Thus $\beta = t + u + w + v = 5.98 \cdot 10^{-8}$ mole/liter of Complexon III, which leads to an error

$$\Delta = \frac{(5{,}98 \cdot 10^{-8} + 7{,}8 \cdot 10^{-9}) \cdot 10^{2}}{10^{-2}} = 6{,}8 \cdot 10^{-4}\ \%$$

It is obvious that in other similar cases, the error may be greater.

Since successive titration of metal ions by means of complexons is not always possible, various methods are used for their removal; the method most often used is precipitation, which, in particular, requires calculation excess precipitant which will prevent interaction between the complexon and the precipitated material. Let us assume, for example that before determining Ca^{2+} or Mg^{2+} by means of Complexon III, zinc ions are removed as ZnS, the question is what $[S^{2-}]$ should be, for example at $c_{Na_2H_2R} = 10^{-3}$ and pH 12.5, so that not more than 0.01% of Complexon III will be expended for dissolving the ZnS. It has been shown that at a pH of 12.5, R^{4-} ions predominate, this means [13]

$$\begin{array}{c} \mathrm{ZnS} \rightleftarrows \mathrm{Zn}^{2+} + \mathrm{S}^{2-} \quad 10^{-22{,}9} \\ \mathrm{Zn}^{2+} + \mathrm{R}^{4-} \rightleftarrows \mathrm{ZnR}^{2-} \quad (10^{-16{,}15})^{-1} \\ \hline \mathrm{ZnS} + \mathrm{R}^{4-} \rightleftarrows \mathrm{S}^{2-} + \mathrm{ZnR}^{2-} \quad 10^{-6{,}75} \end{array}$$

with

$$\begin{array}{c} 10^{-3} \quad x \\ 10^{-3} - 10^{-7} \quad x + 10^{-7} \quad 10^{-7} \end{array}$$

and, according to the law of mass action $10^{-7}(x + 10^{-7}) = 1.8 \cdot 10^{-7} \cdot 10^{-3}$, from which $x = c_{S^{2-}} = 1.8 \cdot 10^{-3}$, i.e. and S^{2-} excess concentration of $2 \cdot 10^{-3}$ mole/liter should be sufficient for the separation.

It has been suggested [1, p.58] that in a similar way, at pH 10 it should be possible to determine Mg^{2+} ions, after preliminary precipitation of Ca^{2+} as the oxalate. Since calculations show that CaC_2O_4 should dissolve in Complexon III at pH 10, this method gives rise to doubt although Arkhangel'skaya has given a detailed procedure for such a separation [15]. Using Arkhangel'skaya's results it is possible to calculate that, for example, during the simultaneous presence of $2.0 \cdot 10^{-3}$ mole/liter of Ca^{2+} and $1.8 \cdot 10^{-3}$ mole/liter of Mg^{2+}, the system should contain at a pH of 10, $c_{C_2O_4^{2}} = 5.1 \cdot 10^{-3}$ and $c_{H_2E} = 2.5 \cdot 10^{-5}$. Here again NaH_2E is eriochrome black ET-00 while the $C_2O_4^{2-}$ is hydrolyzed at the most to the extent of 0.02%. In such a system the following equilibria must be taken into account

$$\mathrm{Mg}^{2+} + \mathrm{H_2O} \rightleftarrows \mathrm{MgOH}^+ + \mathrm{H}^+ \qquad pK_1 = 10{,}7 \tag{59}$$

$$\mathrm{HE}^{2-} \rightleftarrows \mathrm{H}^+ + \mathrm{E}^{3-} \qquad pK_{13} = 11{,}52 \tag{60}$$

$$\mathrm{HR}^{3-} \rightleftarrows \mathrm{H}^+ + \mathrm{R}^{4-} \qquad pK_{24} = 10{,}26 \tag{61}$$

$$\mathrm{MgR^{2-} \rightleftarrows Mg^{2+} + R^{4-}} \qquad pK = 8{,}69 \tag{62}$$

$$\mathrm{MgE^{-} \rightleftarrows Mg^{2+} + E^{3-}} \qquad pK_2 = 5 \text{ at pH } 10 \tag{63}$$

$$\mathrm{Mg(C_2O_4)_2^{2-} \rightleftarrows MgC_2O_4 + C_2O_4^{2-}} \qquad pK_3 = 0{,}95 \tag{64}$$

$$\mathrm{MgC_2O_4 \rightleftarrows Mg^{2+} + C_2O_4^{2-}} \qquad pK_4 = 3{,}43 \tag{65}$$

$$\mathrm{CaC_2O_4 \rightleftarrows Ca^{2+} + C_2O_4^{2-}} \qquad pP = 8{,}75 \tag{66}$$

$$\mathrm{CaR^{2-} \rightleftarrows Ca^{2+} + R^{4-}} \qquad pK_5 = 10{,}59 \tag{67}$$

$$\mathrm{Ca^{2+} + H_2O \rightleftarrows CaOH^{+} + H^{+}} \qquad pK_6 = 12{,}7, \tag{68}$$

since there are indications of the existence of oxalate complexes of magnesium [16].

Using the designations $c_{\mathrm{Mg^{2+}}} = 1.8 \cdot 10^{-3} = c$, $c_{\mathrm{C_2O_4^{2-}}} = 5.1 \cdot 10^{-3} = c_1$,

$$c_{\mathrm{H_2E^-}} = 2{,}5 \cdot 10^{-5} = c_2,\; c_{\mathrm{Ca^{2+}}} = 2{,}0 \cdot 10^{-3} = c_3,\; [\mathrm{H^+}] = 10^{-10} = h,\; [\mathrm{Mg^{2+}}] = x,$$
$$[\mathrm{MgOH^+}] = y,\; [\mathrm{HE^{2-}}] = z,\; [\mathrm{E^{3-}}] = u,\; [\mathrm{HR^{3-}}] = v,\; [\mathrm{R^{4-}}] = w,$$
$$[\mathrm{MgR^{2-}}] = t,\; [\mathrm{MgE^{-}}] = s,$$
$$[\mathrm{Mg(C_2O_4)_2^{2-}}] = q,\; [\mathrm{MgC_2O_4}] = p,\; [\mathrm{C_2O_4^{2-}}] = r,\; [\mathrm{Ca^{2+}}] = n,$$
$$[\mathrm{CaR^{2-}}] = m,\; [\mathrm{CaOH^+}] = l$$

and designating the number of moles of $\mathrm{CaC_2O_4}$ precipitate in 1 liter of solution by Δ, and $c_{\mathrm{HR^{3-}}} = \varphi$, at which value the solutions has a pure blue color, we get the following system of equations

$$hy = K_1 x \tag{69}$$
$$hu = K_{13} z \tag{70}$$
$$hw = K_{24} v \tag{71}$$
$$xw = Kt \tag{72}$$
$$xu = K_2 s \tag{73}$$
$$pr = K_3 q \tag{74}$$
$$xr = K_4 p \tag{75}$$
$$nr = P \tag{76}$$
$$nw = K_5 m \tag{77}$$
$$c = x + y + t + s + q + p \tag{78}$$
$$c_2 = z + u + s \tag{79}$$
$$\varphi = v + w + t' + m \tag{80}$$
$$z = 10(s + u) \tag{81}$$
$$hl = K_6 n \tag{82}$$
$$c_1 - c_3 = c_4 = 2q + p + r - (n + m + l), \tag{83}$$

here equation (81) is the limiting conditions for a pure blue-colored solution, and equation (83) is obtained by excluding Δ from the material balance equations

$$c_1 = 2q + p + r + \Delta, \quad c_3 = n + m + l + \Delta.$$

From equations (81), (79), (70), (73), and (69) we find $z = [\mathrm{HE^{2-}}] = 2.3 \times 10^{-5}$, $u = \mathrm{E^{3-}}] = 6.9 \cdot 10^{-7}$, $s = [\mathrm{MgE^-}] = 1.6 \cdot 10^{-6}$, $x = [\mathrm{Mg^{2+}}] = 2.3 \times 10^{-5}$, $y = [\mathrm{MgOH^+}] = 4.6 \cdot 10^{-6}$. Equations (74), (75), and (78) lead us to the equations $p = xr/K_4$, $q = xr^2/K_3K_4$ and $t = c_5 - ar(r + K_3)$, where $c_5 = c - (x + y + s) = 1.771 \cdot 10^{-3}$ and $a = x/K_3K_4 = 0.5538$.

From equations (76), (82), (72), and (77) in a similar way we get $n = P/r$, $l = K_6P/hr$, $w = K[c_5 - ar(r + K_3)]/x$ and $m = KP[c_5 - ar(r + K_3)]/K_5rx$. Substitution of all these expressions in equation (83) leads to an equation of the third order with respect to r

$$2hK_5x^2r^3 + hK_3[K_5x(x + K_4) + aKK_4P]r^2 -$$
$$- h\,K_3K_4(c_4K_5x - aKK_3P)r - K_3K_4P[K_5x(h + K_6) + c_5hK] = 0, \tag{84}$$

which, after substitution of the letter designations by numerical values , and the usual transformations, leads in the given instance to the equation

$$r^3 + 0{,}9623r^2 - 2{,}456\cdot 10^{-3}r - 9{,}788\cdot 10^{-6} = 0,$$

from which

$$r = [C_2O_4^{2-}] = 4{,}696\cdot 10^{-3},\ p = [MgC_2O_4] = 2{,}9\cdot 10^{-4},$$

$$q = [Mg\,(C_2O_4)_2^{2-}] = 1{,}2\cdot 10^{-5},$$

$$n = [Ca^{2+}] = 3{,}8\cdot 10^{-7},\ l = [CaOH^+] = 3{,}5\cdot 10^{-12},\ t = [MgR^{2-}] =$$

$$= 1{,}467\cdot 10^{-3},$$

$$w = [R^{4-}] = 1{,}3\cdot 10^{-7},\ m = [CaR^{2-}] = 1{,}9\ 10^{-3},\ v = [HR^{3-}] = 2{,}4\cdot 10^{-7}$$

and, finally, $\varphi = c + 1.6\cdot 10^{-3}$, which amounts to an error of about 88%. It should be emphasized that the magnitude of the error found depends on the accuracy of the constants used for calculation. The errors which arise are connected with the approximately 95% solubility of CaC_2O_4 in Complexon III when working under equilibrium conditions. Presumably, the method could be used after removal of the CaC_2O_4 precipitate or by carrying out the titration in the presence of an organic liquid immiscible with water. The technique recommended by Z. V. Arkhangel'skaya, i.e. titrating to the first blue color is, in general, not suitable for accurate work, while for approximate determinations, the kinetics of the dissolution of CaC_2O_4 in the complexon should be verified by investigation, or a detailed statistical study should be made of the method.

SUMMARY

The application of the theory of ionic exchange for evaluating the accuracy of complexometric titration involving metallo-indicators has been considered, as well as its application to establishing the possibility of carrying out successive titration of two metal ions, and determining one ion after precipitation of the other by a suitable reagent.

Calculations of the color intensity in systems containing equivalent initial concentrations of metal ions and complexons are presented, together with calculations of the initial concentration of the complexon which will guarantee a given color.

A study has been made of the successive titration of two metal ions which react with the same reagent: 1) for a pH at which the hydrolysis of the anion of the complexon can be disregarded, while hydrolysis of both ions is taken into account, and 2) for a pH at which the hydrolysis of the complexon anion and one of the metal ions is taken into account.

General methods are given for calculating the results of complexometric titrations for systems containing masking and precipitating reagents.

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LOW-MELTING EXTRACTING AGENTS IN ANALYTICAL CHEMISTRY

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Extraction of elements in the form of their oxonium salts by means of oxygen-containing solvents is used very often in analytical chemistry practice. Such extraction makes it possible to achieve a fairly complete removal of those elements which are present in the form of hydrophobic anions such as $FeCl_4^-$, $SbCl_6^-$, BiI_4^-, $InBr_4^-$, and others.

For each oxygen-containing solvent, and for each individual element, there exists an optimum acidity ensuring the best extraction when extraction is carried out according to an oxonium mechanism [1]. Thus, gold, in the form of a salt of the bromide anion, is most completely extracted by means of diethyl ether from 0.5-4 N HBr, and indium from 4-6 N HBr, while iron is only extracted to the extent of 70% from 5 N HBr, and is hardly extracted at all from 0.5 N HBr by diethyl ether [2]. In the same way, under various conditions of acidity, elements are also extracted from hydrochloric acid solutions [3]. Iron and gold can be separated by extracting them by means of diethyl ether from 0.5 N HBr, but not from 4-5 N HBr.

Elements which form inorganic complex anions can be extracted at certain acidities not only in the form of oxonium salts, but also in the form of ammonium salts by means of amines.

The optimum acidity for each solvent is determined by the different capacity of the individual oxygen-containing solvents or amines to dissolve in aqueous solutions of acids to form the salts of oxonium or ammine cations. Extraction of elements by means of an oxonium mechanism is usually carried out at fairly high acidities. Ammine cations are very stable, and, accordingly, a weakly acid medium is sufficient for their formation as a rule. It does not follow, however, that all amines can extract salts of inorganic anions from weakly acid media, and that all oxygen-containing solvent require high acidity. Extraction can readily occur at acidities when only part of the solvent is converted into the salt of the oxonium or ammine cation. Since these salts are, usually, readily soluble in water, the acidity which is suitable for extraction is that at which the extracting agent is about 10-20% more soluble in the acid phase than in pure water. It is readily understood that when the acidity is so high that the extracting agent is completely converted into the salt of the corresponding cation and dissolves in the aqueous phase, extraction becomes impossible. Sometimes, however, extraction can still be carried out even under these conditions, when indifferent solvents such as dichloroethane, chloroform and others are added to the extracting solvent. This, for example, is true for the case of the extraction of niobium from concentrated hydrochloric acid media by means of a mixture of methyldioctylamine and xylene [4], and for the separation of niobium and tantalum by extraction with a solution of tribenzylamine and chloroform [5].

By having at one's disposal a selection of various oxygen-containing solvents and amines, it is possible to realize extraction over a wide range of acidities. The latter will be useful for a more successful extraction separation of the elements, since formation of the the requisite complex anions by the various elements, the salts of which are readily extracted, occurs at different acidities. Thus, quadrivalent selenium and tellurium, at low acidities, form hydrophilic anions SeO_3^{2-} and TeO_3^{2-}, while in a medium of concentrated hydrochloric acid tellurium gives a hydrophobic anion $TeCl_6^{2-}$ and the selenium remains in the form of SeO_3^{2-}. This difference has already been used for detecting tellurium in the presence of selenium [6]. Tellurium and selenium, apparently, could be separated by extraction from concentrated hydrochloric acid; during extraction from 6N HCl only 34%

tellurium is extracted and the separation is difficult to carry out [7]. Accordingly, for effective separation of selenium and tellurium it would be useful to have an extracting agent capable of extracting from a medium of concentrated hydrochloric acid, where, for example, diethyl ether is not suitable.

Such considerations could be advanced for a number of other extraction separations. All that has been said emphasizes the desirability of having a choice of extracting agents embracing a wide range of acidities at the disposal of the analyst.

As indicated already [8], for the rapid extraction separation of elements it is very convenient to use solid but low-melting organic materials, or their mixtures with the usual organic solvents, as extracting agents. Such an extraction is carried out in slightly heated solutions when the extracting agent is molten. After extracting and then cooling under the tap, the extracting agent rapidly solidifies into a continuous mass which adheres to the vessel walls, and the aqueous layer can be removed simply by pouring it off. Extraction with low-melting materials does not require the use of a separating funnel.

TABLE 1

Recommended Selection of Low-Melting Mixtures for Extraction of Elements Over a Wide Acidity Range – from pH 3.7 to 18 N (HCl + H_2SO_4).

All mixtures contain about 25% paraffin. At 60° they are liquid, at 20° they are semi-solid•

Composition of the mixture	Acidity range for which the mixture is suitable		Efficiency of the mixture, taking extraction of Fe and Cd••as examples	
	Original normality	Equilibrium		
Dimethylaniline + paraffin	1—2	pH 3,7—3,4	20—1,5	Cadmium
α-Naphthylamine	0,3—1	pH 3,6—3,3	70—> 70	
o-Chloraniline + paraffin	0,1—2	pH 3,7—1,8	2—170	
Methyl ethyl ketone + paraffin . . .	0,1—4	0,1—3,3 N	6—400	Iron
Cyclohexanone + paraffin	0,1—5	0,1—4 N	5—5000—1000	
Diethyl ketone + paraffin	2—9	2—6,4 N	10—450 —100	
Methyl butyl ketone + paraffin . . .	4—10	4—7 N	15—2000—30	
Methyl isobutyl ketone + paraffin	3—10	3—7,2 N	20—2000—200	
Propyl acetate + paraffin	5—8	5—7 N	17—75	
Butyl acetate + paraffin	4—9	4—8 N	10—75	
Amyl acetate + paraffin	8—11	8—9 N	300—500—200	
Ethyl butyrate (the ethyl ester of butyric acid) + paraffin	6—11	6—9 N	8—200	
Ethyl isovalerate (the ethyl ester of isovaleric acid) + paraffin	9—20	9—17 N	50–500	
Ethyl benzoate + paraffin	10—20	10—18 N	> 80–1000	

The present article contains a description of a selection of low-melting extracting agents which are suitable for work at varying acidities. The recommended extracting agents were found as a result of a study of the extraction of iron ($FeCl_4^-$) and cadmium (CdI_4^-). Iron and cadmium were chosen because the complex ions indicated are stable over a fairly wide range, so that it was possible to study a wide range of acidities. The good partition coefficients obtained for these elements give a basis for postulating that mixtures are also suitable for the extraction of other elements, as long as the latter are capable of forming readily extractable salts of complex anions in the acidity range studied. Another criterion of the suitability of the mixtures tested for extracting over a given acidity range is the appreciable increase in their solubility – 5-20% – over their solubility in pure water.

Extraction with Mixtures of Oxygen-Containing Solvents and Paraffin

Many liquid esters and ketones which readily extract certain elements, form solid or semisolid mixtures

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•The volumes of the amines or oxygen-containing solvents taken were equal to the volume of solution being extracted.

••Partition coefficients are given. Where three figures are given the middle one refers to the maximum coefficient observed at an intermediate acidity.

on addition of a small amount of paraffin (about 25%). These mixtures which readily fuse into a readily mobile liquid on gentle heating, on cooling solidify to a thick mass which adheres to the vessel walls.

The mixtures studied proved to be suitable for the extraction of elements from media with acidities ranging from 0.1-20 N.

During the extraction of iron from 0.1-5 N hydrochloric acid solutions, the chloride ion concentration necessary for the formation of the chloride anion was achieved by addition of a 20% solution of NH_4Cl. The concentration of 20 N in the solution being extracted was established by using a mixture of hydrochloric and sulfuric acids.

Extraction of iron by mixtures of oxygen-containing solvents and paraffin was carried out as follows. To a test tube containing 2 ml of a solution of ferric chloride in hydrochloric acid (or in a mixture of sulfuric and hydrochloric acids) of a definite normality, and containing usually about 5 mg of iron and 400-800 mg of chloride ions, was added 2 ml of the ester or ketone under test, followed by about 0.6 g of paraffin. The latter was melted by heating the test tube in a water bath, and the test tube shaken for 1-2 minutes, the mixture was then cooled under the tap. The aqueous layer was removed from the extract which solidified on the test tube walls, by simply pouring it off; the extract was melted again, and then in order to re-extract the iron, it was shaken with added water. The iron content of aliquots of the aqueous layer and re-extract were determined by means of sulfosalicylic acid, and from the results obtained the partition coefficients calculated. In parallel with this, a sample of the aqueous layer was taken and the equilibrium acidity of the extracting solution determined by titration with 0.1 N potassium hydroxide. As a result of the extraction of some free hydrochloric acid by the solvent, and also as a result of an increase in the volume of the aqueous layer during extraction from fairly concentrated solutions of acids, the equilibrium concentration of the acid was always somewhat lower than the original concentration.

Extraction with Low-Melting Amines or With Mixture of Liquid Amines and Paraffin.

For extracting certain elements from weakly acid, almost neutral solutions, it is possible to use amines; in such cases, the weaker the amine as a base, the more acid the medium it can be used for extracting.

Of the amines tested, the most suitable for extracting elements in weakly acid regions proved to be α-naphthylamine (m.p. 50°) and a mixtures of methylaniline or o-chloraniline with paraffin. The latter, on heating, form homogeneous liquids, while on cooling to room temperature they solidify to give a continuous mass. The extractive capacity of the extracting agents chosen was studied taking as an example the extraction of salts of the iodide anion of cadmium. Extraction was carried out as follows.

Into a test tube with 1 ml of cadmium nitrate solution containing 10 mg of Cd and acidified with hydrochloric acid to the requisite acidity, was added 1 ml of 20% ammonium iodide solution. 2 g of α-naphthylamine or 2 ml of liquid amine followed by 0.6 of paraffin were then added. The test tube was heated on a water bath, shaken for 1-2 minutes, and then cooled. The aqueous layer was poured into another test tube and two aliquots taken from it. The cadmium content of one of the aliquots was determined by colorimetric measurement of the color of the suspension of cadmium sulfide,* while in the other the pH, which differed appreciably from the original pH, was measured.

The results obtained during extraction with mixtures of oxygen-containing solvents or amines with paraffin are given in Table 1.

Recommended Low-Melting Mixtures and Their Characteristics

It is readily seen that the low-melting extracting agents tested make it possible to work over a very wide acidity range, starting at pH 3.7 and ending at 17-18 N, each individual mixture being most suitable for extraction over a particular acidity range (Table 2).

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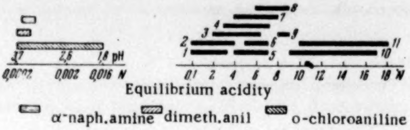
*Since the partition coefficient for CdI_4^{2-} was fairly high in almost all the experiments, and also because of the difficulty of determining cadmium in the organic layer, its content in the latter was not determined, and the partition coefficient was calculated on the basis of the cadmium content of the aqueous layer.

TABLE 2

Acidity Ranges for which Low-Melting Mixtures of Organic Solvent and Paraffin are Suitable



To the left — amines; to the right oxygen-containing solvents

1) Methyl ethyl ketone; 2) Cyclohexanone; 3) Diethyl ketone; 4) Methyl isobutyl ketone; 5) Methyl butyl ketone; 6) Propyl acetate; 7) Butyl acetate; 8) Ethyl butyrate; 9) Isoamyl acetate; 10) Ethyl isovalerate; 11) Ethyl benzoate.

Methods for Preparing the Mixtures

Two methods can be used when using mixtures of organic solvents and paraffin. Three parts of solvent and one part of paraffin can be mixed beforehand on heating, and the solid mixture formed stored in a flask with a ground-glass stopper, a known amount being taken out with a spatula as required. This variant is not very suitable, because on storing for some days there is a tendency to formation of layers. In such an event the mixture should be melted again and cooled prior to use.

In the second variant, the liquid solvent is added directly to the solution to be extracted contained in the vessel to be used for extraction, and a portion of paraffin then added, the amount of the latter being assessed either visually or by approximate weighing. The drawback of this method is that the error involved in only making an approximate estimate of the amount of paraffin added may affect the ease with which the resultant mixture melts, and affect the partition coefficient of the element to be extracted. After some practice, however, a mixture can be prepared fairly rapidly and accurately.

Characteristics of the Mixtures

a) Mixtures of paraffin and amines dimethylaniline or o-chloraniline), and pure α-naphthylamine are suitable for extracting elements from weakly acid media, the equilibrium acidity of which varies within the limits pH 3.7 to pH 1.8. They cannot be used for extracting elements with readily hydrolyzable cations such as: Nb, Ta, Sn, Sb, Fe, and Zr since they are precipitated at low acidities.

α-Naphthylamine and mixtures of o-chloraniline and paraffin are readily oxidized, accordingly iron cannot be extracted by means of them, since under these conditions iron is reduced to the nonextractable divalent state. Because of the ease with which they can be oxidized, the extracting agents described are almost invariably dark in color.

b) Mixtures of paraffin and oxygen-containing solvents. Almost all the recommended mixtures are reasonably stable to oxidizing agents. Mixtures of paraffin and cyclohexanone are exceptional in that they are readily oxidized. Accordingly, such elements as vanadium (V) and chromium (VI) which can only be extracted in higher valence states, are difficult to extract with such a mixture.

Depending on the acidity * of the solution being extracted, the following oxygen-containing solvents, mixed with 25 % of paraffin * *, are suitable for extraction:

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*Equilibrium acidities are quoted.

* *In addition to extraction on the basis of an oxonium mechanism, the low-melting mixtures recommended can also be used when extractions of elements based on other mechanisms are carried out.

from 0.1-1 N	Methyl ethyl ketone, cyclohexanone
2N	Methyl ethyl ketone, cyclohexanone, and diethyl ketone
3N	Methyl ethyl ketone, cyclohexanone, diethylketone, methyl isobutyl ketone
4N	Methyl butyl ketone, cyclohexanone, diethyl ketone, methyl isobutyl ketone, butyl butyl acetate
5N	Methyl butyl ketone, propyl acetate, diethyl ketone, methyl isobutyl ketone, butyl acetate
6N	Methyl butyl ketone, propyl acetate, diethyl ketone, methyl isobutyl ketone, ethyl butyrate
7N	Methyl butyl ketone, propyl acetate, methyl isobutyl ketone, butyl acetate, ethyl butyrate
8N	Amyl acetate, butyl acetate, ethyl butyrate
9N	Amyl acetate, ethyl isovalerate, ethyl butyrate
10-17N	Ethyl benzoate, ethyl isovalerate

During the extraction of elements from 0.1-5 N acid solutions, in order to increase the partition coefficients, the ions of the corresponding halide in the form of the ammonium, sodium, or potassium salts should be added to the solution being extracted.

SUMMARY

Solid, low-melting extracting agents facilitate extraction separation of elements, since they permit extraction to be carried out in simple flasks or test tubes, there being no need to resort to the use of separating funnels.

A selection of such low-melting extracting agents is suggested which permits extractions of elements from solutions with acidities ranging from pH 3.7 to 17-18 N. α-Naphthylamine, and a mixture of dimethylaniline or o-chloraniline with paraffin, are suitable for extracting from weakly acid solutions, while starting at 0.1 N acid solutions, a mixture of an oxygen-containing solvent and paraffin is suitable.

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A STUDY OF THE DISSOCIATION OF ARSENAZO (BENZENE-2-ARSONIC ACID - (1-AZO-2)-1,8-DIHYDROXYNAPHTHALENE-3,6-DISULFONIC ACID)

A. E. Klygin and V. K. Pavlova

During the study of the dissociation processes of weak polybasic acids, potentiometric and spectrophotometric methods of investigation are often used; these were the methods that we used in the course of the work described here.

Arsenazo was purified by double recrystallization from an aqueous solution of distilled hydrochloric acid, and dried at room temperature. The percentage purity of the preparation was checked on the basis of its absorption spectra [1].

The stock solution of $4.7 \cdot 10^{-2}$ M arsenazo was prepared by dissolving an exact aliquot of arsenazo. All the measurements of the optical density were carried out on a nonrecording quartz SF-11 spectrophotometer using cells from a photocolorimeter.

Potentiometric titration and measurements of the hydrogen ion concentration were carried out electrometrically on a setup including a PPTV-1 potentiometer, a saturated calomel electrode as the reference electrode and a quinhydrone or glass electrode; in the latter case a LU-2 tube amplifier was used. The accuracy of the measurements was ±0.05 pH units. Experiments were carried out at 20± 0.5°.

All the experimental results were subjected to statistical treatment [2-4] with a confidence level of $\alpha = 0.95$.

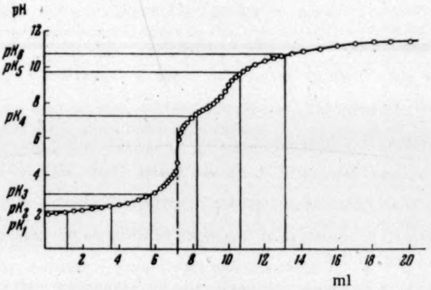

Fig. 1. Potentiometric titration curve of 5 ml of $4.7 \cdot 10^{-2}$M arsenazo solution with $9.79 \cdot 10^{-2}$ M KOH solution.

Potentiometric titration showed that the equivalence point corresponds to the point at which all three hydrogen ions are neutralized. The normality of the stock solution as determined by potentiometric titration was found to be $4.7 \cdot 10^{-2}$ M.

For an approximate evaluation of the pK of the acid, the pH of a solution of acid half neutralized with alkali was used [5].

According to the results of the neutralization curves (Fig. 1), it follows that the order of the first three constants are similar to each other and equal to 10^{-2} - 10^{-3}. The order of the fourth constant differs sharply from the orderof the first three constants and from the last two and is given by $K_4 = 10^{-8}$. The values of the last two constants are similar to each other and are of the order of 10^{-11} - 10^{-12}.

The closeness of the values of the first three and the last two dissociation constants of arsenazo did not permit their quantitative determination potentiometrically. Accordingly, further investigations of this reagent were carried out by a spectrophotometric method.

Arsenazo is a weak hexabasic acid. The bright-red color of its aqueous solution changes in relation to the pH, from a raspberry color in alkaline media to a violet in sulfuric and perchloric acid media [6].

Absorption curves for a $2\ 10^{-5}$ M solution of arsenazo, taken at various pH's of the solution (Fig. 2), confirmed the effect of the pH of the solution on the positions at which the absorption maxima are located, and on the character of the absorption curve. Spectrophotometric studies of the dissociation processes were carried out on the basis of the results of the curves of "optical density – pH" ("D–pH") at 370, 500, 520, and 570 mμ. This choice of wave lengths made it possible to work at the points of maximum absorption, and in those parts of the spectra which are more sensitive to changes in the concentration of the acid or alkaline forms of the anions of the given dye.

The most noticeable change in the optical density on the five parts of the "D–pH" curves (Figs. 3,4,5)can be explained on the basis of the existence of the following processes:

Section	pH	Reactions	
OR	0– 2	$H_6R \rightleftarrows H_5R^- + H^+$	$K_1,\ \varepsilon_1$
		$H_5R^- \rightleftarrows H_4R^{2-} + H^+$	$K_2,\ \varepsilon_2$
AD	2,5– 5,2	$H_4R^{2-} \rightleftarrows H^3R^{3-} + H^+$,	$K_3,\ \varepsilon_3$
CB	6,5– 9,2	$H_3R^{3-} \rightleftarrows H_2R^{4-} + H^+$,	$K_4,\ \varepsilon_4$
EF	9,2–11,4	$H_2R^{4-} \rightleftarrows HR^{5-} + H^+$,	$K_5,\ \varepsilon_5$
NM	11,6–12,5	$HR^{5-} \rightleftarrows R^{6-} + H^+$,	$K_6,\ \varepsilon_6$

For calculating the molar extinction coefficients (ε) and dissociation constants (K) of the reagent behaving as an indicator, the method suggested by Komar' was used [7].

All calculations were carried out on the basis of measurements of the optical density (D) and the pH of the solutions according to equations (1), (2), (3), and (4), which hold for different experiments at constant wavelength and temperature:

$$K = \frac{(D_l h_l - D_p h_p)(h_l - h_m) - (D_l h_l - D_m h_m)(h_l - h_p)}{(h_l - h_p)(D_l - D_m) - (h_l - h_m)(D_l - D_p)}, \qquad (1)$$

$$\varepsilon_n = \frac{(D_l h_l - D_p h_p)(D_l - D_m) - (D_l h_l - D_m h_m)(D_l - D_p)}{Cl\,[(h_l - h_p)(D_l - D_m) - (h_l - h_m)(D_l - D_p)]}, \qquad (2)$$

$$\varepsilon_{n+1} = \frac{D_l D_m h_p (h_l - h_m) + D_m D_p h_l (h_m - h_p) - D_l D_p h_m (h_l - h_p}{Cl\,[(h_l - h_m)(D_l h_l - D_p h_p) - (h_l - h_p)(D_l h_l - D_m h_m)]} \qquad (3)$$

or

$$\varepsilon_{n+1} = \frac{D_l (K + h_l)}{KCl} - \frac{h_l \varepsilon_n}{K}, \qquad (4)$$

where ϵ_n and ϵ_{n+1} are the molar extinction coefficients for ions with charges of n and n + 1; K is the dissociation constant for the reaction $H_{(8-n)} \rightleftharpoons H_{(8-n-1)}R^{(n+1)} + H^+$; C is the original concentration of arsenazo ($1.4 \cdot 10^{-5}$M); 2 is the cell length (2 cm); $D_{l,\,m,p}$ are the optical densities in experiments l, m, p; and $h_{l,m,p}$ the hydrogen ion concentrations in experiments l, m, p. Because there is a slight increase in optical density on sections OR and AD (Figs. 3,4,5), calculations of the values of K_1, K_2, and K_3 did not give positive results for the given series of experiments. Determination of the values of K_4, K_5, and K_6 were carried out on the basis of the results of "D – pH" curves (Table 1) for the parts designated on Figs. 3, 4 and 5 by CB, EF, and NM. Results of these calculations are given in Table 2. The results given in the Table show good agreement between the values given below for K_4, K_5, and K_6 and calculated by various methods for experimental points at different wave lengths, and the values of the molar extinction coefficients ϵ_3, ϵ_4, and ϵ_5 at 500 mμ. This confirms the existence of different forms of the arsenazo anions and the correctness of the method of calculation used.

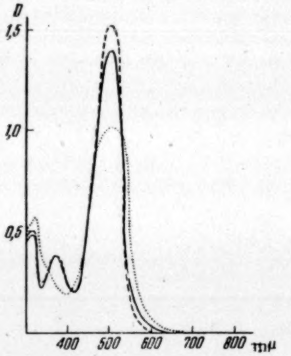

Fig. 2. Absorption curves for $2.4 \cdot 10^{-5}$M arsenazo solution at various pH's
– – – – pH 1.2; ——— pH 6 3 ... 10.36.
(cell 3 cm)

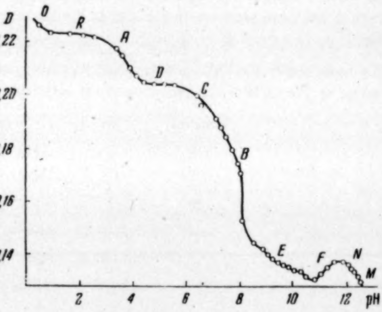

Fig. 3. "D – pH" curve at 370 mμ

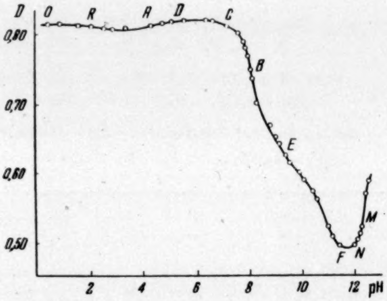

Fig. 4. "D – pH" curve at 500 mμ

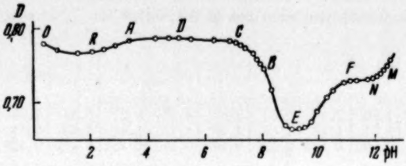

Fig. 5. "D – pH" curve at 520 mμ.

TABLE 1

Results of the "D – pH" Curves at 370, 500, and 520 Taken for Calculation

Value / Nos.	14	15	16	17	18	25	26	27
pH	7,09	7,25	7,45	7,70	7,85	9,50	9,77	10,00
D_{500}	0,814	0,810	0,802	0,790	0,782	0,608	0,600	0,590
D_{520}	0,786	0,783	0,778	0,77	0,765	0,667	0,676	0,688
D_{370}	0,191	0,188	0,184	0,179	0,176	0,137	0,135	0,134

Value / Nos.	28	29	30	33	34	35	36	37
pH	10,35	10,49	10,95	11,90	12,04	12,12	12,22	12,35
D_{500}	0,570	0,559	0,519	0,490	0,498	0,504	0,516	0,566
D_{520}	0,710	0,720	0,730	0,736	0,740	0,741	0,741	0,748
D_{370}	0,133	0,131	0,130	0,137	0,136	0,135	0,134	0,132

TABLE 2

Results of the Calculations of K_4, K_5, and K_6 and of ϵ'_4, ϵ_5, and ϵ_6 by Means of Equations (1), (2), (3), and (4)

Calculation for the points	$K_n - \bar{K}_n \pm \frac{t_\alpha \cdot \delta}{\sqrt{n}}$	$\epsilon_n - \bar{\epsilon}_n \pm \frac{t_\alpha \cdot \delta}{\sqrt{n}}$	$\epsilon_{n+1} - \epsilon_{n+1} \pm \frac{t_\alpha \cdot \delta}{\sqrt{n}}$
14, 15, 16, 17, 18 At 370 mμ	$K_4=(3{,}3\pm0{,}5)\cdot10^{-8}$	$\varepsilon_3=(7{,}2\pm0{,}07)\cdot10^3$	$\varepsilon_4=(5{,}9\pm0{,}0)\cdot10^3$
14, 15, 16, 17, 18 At 500 mμ	$K_4=(1{,}2\pm0{,}2)\cdot10^{-8}$	$\varepsilon_3=(2{,}9\pm0{,}06)\cdot10^4$	$\varepsilon_4=(2{,}56\pm0{,}07)\cdot10^4$
14, 15, 16, 17, 18 At 620 mμ	$K_4=(1{,}4\pm0{,}2)\cdot10^{-8}$		
25, 26, 28, 29, 30 At 500 mμ	$K_5=(2{,}3\pm0{,}4)\cdot10^{-11}$	$\varepsilon_4=(2{,}2\pm0{,}03)\cdot10^4$	$\varepsilon_5=(1{,}85\pm0{,}02)\cdot10^4$
25, 26, 27, 28, 29 At 520 mμ	$K_5=(3{,}5\pm0{,}4)\cdot10^{-11}$		
33, 34, 35, 36 At 500 mμ	$K_6=(3{,}4\pm2{,}8)\cdot10^{-13}$	$\varepsilon_5=(1{,}6\pm0{,}004)\cdot10^4$	$\varepsilon_6=(2{,}23\pm0{,}03)\cdot10^4$
33, 34, 36, 37 At 520 mμ	$K_6=(9{,}2\pm6{,}5)\cdot10^{-13}$		

TABLE 3

Results of the "D – pH" Curves at 370 and 570 mμ. Taken for Calculation (The results of these calculations are given in Table 4)

Value / Nos.	1	2	3	4	5	6	7	8	9	10
pH	1,76	2,40	2,63	2,81	3,02	3,27	3,41	4,28	5,50	6,03
D_{370}	1,51	1,48	1,47	1,45	1,43	1,41	1,40	1,34	1,32	1,32
D_{570}	0,406	0,433	0,438	0,443	0,449	0,454	0,460	0,469	0,470	0,481

TABLE 4

Results of Calculations of K_3 and ϵ_2 and ϵ_3 by Means of Equations (1), (2), (3), and (4)

Calculations for the points	$K_3 - K_3 \mp \frac{t_\alpha \cdot \delta}{\sqrt{n}}$	$\epsilon_2 - \epsilon_2 \pm \frac{t_\alpha \cdot \delta}{\sqrt{n}}$	$\epsilon_3 - \epsilon_3 \pm \frac{t_\alpha \cdot \delta}{\sqrt{n}}$
3, 4, 5, 6, 7 At 370 mμ	$(1,9 \pm 0,5) \cdot 10^{-3}$	$(8,24 \pm 0,3) \cdot 10^{3}$	$(7,3 \pm 0,04) \cdot 10^{3}$
2, 3, 4, 5, 6 At 570 mμ	$(1,9 \pm 0,8) \cdot 10^{-3}$	$(2,22 \pm 0,02) \cdot 10^{3}$	$(2,43 \pm 0,03) \cdot 10^{3}$

TABLE 5

Results of the "D – pH" Curves at 370 Taken for Calculation (Results of the Calculations are given in Table 6)

Values / Nos.	1	2	3	4	5	6	7	8
pH	0,27	0,38	0,51	0,64	0,82	1,05	1,15	1,35
D_{370}	0,392	0,391	0,390	0,389	0,388	0,387	0,386	0,385

A comparison of the "D – pH" curves at wave lengths of 370, 500, and 520 mμ shows the greatest change in optical density on section AD at 370 and 520 mμ. Determination of the value of K_3 was carried out on the basis of the "D – pH" curves at 370 and 570 mμ with the highest arsenazo concentration of $9.4 \cdot 10^{-5}$ M. The results are given in Tables 3 and 4.

The values of ϵ_3 at 370 mμ in Table 4 are in good agreement with the values of ϵ_3 in Table 2; in addition, a comparison of the values of ϵ_2 and ϵ_3 (Table 4) show that the highest value of ϵ_2 is observed at 370 mμ.

Accordingly, determination of the value of the dissociation constants of the first two stages were carried out on the basis of the "D – pH" curves at 370 mμ for solutions with pH 0.2-1.5 and an arsenazo concentration of $9.4 \cdot 10^{-5}$ M. These results are given in Tables 5 and 6.

As the results in Table 5 show, the values of the optical density hardly change at all over the pH range tested. Nevertheless, by choosing a combination of the points furthest removed from each other, it is possible to get values of the dissociation constant which testify to the existence of two stages of dissociation in this pH range.

TABLE 6

Calculation of K_1 and K_2 and of ϵ_0, ϵ_1, and ϵ_2 by Means of Equations (1), (2), (3), and (4) at 370 mμ

No. of points, i m p	$K_1 \cdot 10^1$ according to (1)	$\epsilon_0 \cdot 10^{-3}$ according to (2)	$\epsilon_1 \cdot 10^{-3}$ according to (3)
1,3,5	6,9	8,4	8,3
1,2,4	9,1	8,6	8,4
2,4,5	12,0	8,6	8,4
1,4,5	12,0	8,6	8,0
2,3,5	5,6	8,4	8,2
2,3,4	5,0	8,5	8,0
1,2 5	9,5	8,1	8,1
Mean	$(8,5 \pm 2,6) \cdot 10^{-1}$	$(8,5 \pm 0,1) \cdot 10^3$	$(8,2 \pm 0,2) \cdot 10^3$

No. of points, i m p	$K_2 \cdot 10^2$ according to (1)	$\epsilon_1 \cdot 10^{-3}$ according to (2)	$\epsilon_2 \cdot 10^{-3}$ according to (4)
4,5,7	2,7	8,3	
4,6,7	1,0	8,3	
4,5,8	5,7	8,3	8,3
4,7,8	14,8	8,4	8,2
5,6 8	2,5	8,3	8,2
5,7,8	17,2	8,4	8,1
4,6,8	4,7	8,3	8,1
Mean	$(6,9 \pm 5,9) \cdot 10^{-2}$	$(8,3 \pm 0,08) \cdot 10^3$	$(8,2 \pm 0,09) \cdot 10^3$

TABLE 7

Results of Calculating pH and D

Predominant form of the anion	pH value at the change-over point	$D = \epsilon_n lC$	D, experimental value based on "D–pH" curves
H_5R^-	0,60	$D = 0,390$, $l = 0,5$ cm 370 mμ, $\epsilon_1 = 8,3 \cdot 10^3$, $C = 9,4 \cdot 10^{-5}$ M	0,390
H_4R^{2-}	1,95	$D = 0,385$, $l = 0,5$ cm 370 mμ, $\epsilon_2 = 8,2 \cdot 10^3$, $C = 9,4 \cdot 10^{-5}$ M	0,384
H_3R^{3-}	5,20	$D = 0,813$, $l = 2,0$ cm 500 mμ, $\epsilon_3 = 2,9 \cdot 10^4$, $C = 1,4 \cdot 10^{-5}$ M	0,819
H_2R^{4-}	9,20	$D = 0,616$, $l = 2,0$ cm 500 mμ, $\epsilon_4 = 2,2 \cdot 10^4$, $C = 1,4 \cdot 10^{-5}$ M	0,624
HR^{5-}	11,40	$D = 0,484$, $l = 2,0$ cm 500 mμ, $\epsilon_5 = 1,73 \cdot 10^4$, $C = 1,4 \cdot 10^{-5}$ M	0,488

The values of K and ε obtained can be used for calculating the values of the optical densities for points corresponding to the regions where any one anion of the dye preferentially exists. In order to calculate the pH at which the given form of the anion exists in maximum concentration, it is necessary to take into account the following processes:

$$H_{(6-n)}R^{n-} \rightleftarrows H_{(6-n-1)}R^{(n+1)-} + H^+,\ K_{n+1}$$

$$H_{(6-n-1)}R^{(n+1)-} \rightleftarrows H_{(6-n-2)}R^{(n+2)-} + H^+,\ K_{n+2}.$$

When the initial concentration of the dye is C (mole/liter), while the equilibrium concentrations are — $[H^+] = h$, $[H_{(6-n)}R^{-n}] = v$, $[H_{(6-n-1)}R^{(n+1)-}] = w$, $[H_{(6-n-2)}R^{(n+2)-}] = z$, then

$$K_{(n+1)}v = wh \tag{5}$$

$$K_{(n+2)}w = zh \tag{6}$$

$$C = v + w + z \tag{7}$$

Differentiating equations (5), (6), and (7) with respect to h and equating w' to 0, we get the system of equations:

$$K_{(n+1)}v' = w \tag{8}$$

$$z'h + z = 0 \tag{9}$$

$$v' + z' = 0 \tag{10}$$

By substituting the values of v', z', and z found from (8), (9), and (6) in (10) we find that

$$h = \sqrt{K_{(n+1)}K_{(n+2)}}. \tag{11}$$

Results of the calculations of pH and D given in Table 7 show good agreement between the values of optical density obtained experimentally and by calculation

SUMMARY

The six stages of arsenazo dissociation have been studied, and the values of the dissociation constants and molar extinction coefficients determined (at 370, 500, 520, and 570 mμ).

It has been shown that it is more expedient to use a spectrophotometric method of study for determining the successive dissociation constants of weak organic acids when these constants lie close to each other, provided the corresponding forms of the anion have different molar extinction coefficients.

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A SPECTROPHOTOMETRIC STUDY OF THE COLORED COMPLEXES OF QUADRIVALENT TIN WITH CERTAIN REAGENTS CONTAINING OH GROUPS

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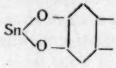
Color reactions and methods for the photometric determination of quadrivalent tin are usually based on the formation of compounds with colored reagents. The light absorption of such compounds is determined by the addendum and not by the central ion of the complex. Colored compounds of tin with alizarin [1], quinalizarin [2], hematoxylin [3], morine [4], quercetin [5], stilbazo [6], hematein [7], and anthrapurpurin and flavopurpurin [8] have been described. All these reagents contain at least two hydroxyl groups in the ortho position.

Nevertheless, as yet, no general criteria for choosing the best of a number of color reagents have been worked out; neither has a comparative study been made of the reagents for tin. We have tried to fill this gap on the basis of a spectrophotometric study of the reactions.

The most important characteristics of a colored complex are its stability and optical properties. Most of the reagents listed above give complexes of reasonable stability with tin. In all cases a chelate bond, develops most often of the type  with a five-membered ring. Accordingly, the complexes of tin with various reagents do not differ very strongly with respect to stability. On the other hand, the effect of complex formation on the conjugation bond of the dye depends essentially on the structure of the latter. The optical effect observed on substituting hydrogen atoms by tin is very strongly developed for various agents.

A comparative study of a series of reagents for tin shows that the optical characteristics are the most important criteria for choosing a reagent of a given type. The sensitivity of a reaction can usually be expressed by the molar light-absorption coefficient (E) of the complex. In addition, the sensitivity and accuracy of a determination depend on the difference between the absorption spectra of the molecular form of the reagent HR and its complex with tin SnR. Finally, the color of all the reagents listed increases (even in the absence of tin) on increasing the pH to a certain limit; accordingly, of great importance is the interval between the pH at which the complex is formed and the pH at which the ionic form (salt) of the dye R^- is formed, the latter being usually intensely colored.

Colored Compounds of Tin with Hydroxyanthraquinones.

The reagents tested were alizarin, quinizarin (1-4-dihydroxyanthraquinone), and quinalizarin (1, 2, 5, 8-tetrahydroxyanthraquinone). Under normal conditions, alizarin forms a very weakly colored compound with quadrivalent tin; its formation is only observable when excess alizarin is extracted with nonaqueous solvents, for example ether.

The compound of tin with quinizarin has an orange color and is sparingly soluble in water, but it can be kept in the form of a colloidal suspension by means of gelatin. The compound is stable at a pH of 4-5. The difference between the optical densities of a solution of the complex and of free quinizarin is insignificant and does not amount to more than 10%. Accordingly, quinizarin cannot be used as a reagent for the photometric determination of tin.

The complex compound of tin with quinalizarin has been described before [9]. For a light-filter with $\lambda_{Eff.} = 496$ mμ, the value of the molar coefficient of light absorption of the molecular form of quinalizarin $E_{HR} = 5 \cdot 10^3$, and of the complex $E_{SnR} = 2 \cdot 10^4$. The great drawback of quinalizarin as a reagent is its extremely low solubility in aqueous solutions. On addition of acetone or alcohol, the solubility of quinalizarin and of its complex with tin increases, on the other hand the difference between the absorption spectra of the reagent and of the complex decreases. Finally, another drawback of quinalizarin is the superposition of its indicator properties: the SnR complex is formed only on increasing the pH to 5-6, while at pH 6 formation of the R^- form of quinalizarin starts.

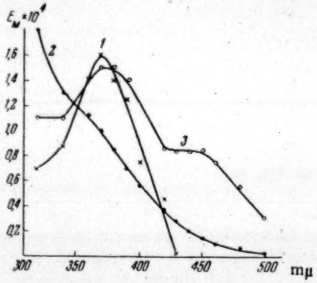


Fig. 1. Absorption spectra of various forms of quercetin:
1) Molecular form (HR); 2) ionic form (R^-);
3) the complex of quercetin with tin (SnR).

The Compound of Quadrivalent Tin with Quercetin

Photometric determination of tin by means of quercetin, according to Liska [5], can be carried out in a solution which is 0.2 N with respect to HCl. The light absorption of solutions of the complex compound formed between tin and quercetin conforms to the Lambert-Beer law. At high tin concentrations it is necessary to construct a calibration curve. According to the same source there is formed a compound with a ratio of tin to quercetin of 3:2.

We used quercetin obtained from onion peel*. Quercetin is sparingly soluble in water but readily soluble in alcohol. The compound of quadrivalent tin with quercetin is also sparingly soluble in water but is considerably more soluble in alcohol. Accordingly, the reaction between Sn^{IV} and quercetin was studied in 50% alcoholic solutions. In acid media at a pH of 1-8, quercetin solutions are colored pale-yellow. At pH ≥ 10 the solubility of quercetin increases and the solutions acquire a bright-yellow color. When such solutions are stood in air the quercetin breaks down and the color of the solutions gradually becomes pale. Formation of a complex of tin with quercetin at concentrations of the components of about $5 \cdot 10^{-5}$M is already observable at a pH of 2 and lower. Nevertheless, on increasing the pH of the solution, the optical density increases several times and attains a constant value at pH 3. Only at pH > 10 does the complex break down appreciably.

Visually, the R^- form of quercetin is similar in color to the SnR form, although the first is considerably weaker in color. This corresponds to the usual relationship. This analogy between the colors of the MeR- and R-forms serves as a physical basis for the theory of "intramolecular dissociation" and for a number of hypotheses regarding the choice of the optimum pH in similar reactions. Nevertheless, a full study reveals a number of characteristics.

In Fig. 1. are shown the absorption of the HR-, SnR-, and R- - forms of quercetin; the curves were obtained by means of a SF-4 spectrophotometer. In the visible part of the spectrum (λ 420 mμ) the absorption curves of the R- and SnR- forms are similar. Nevertheless, the complete absorption spectrum of the R- form (Curve 2) clearly differs from the spectrum of the SnR- form (Curve 3), and is more like the spectrum of the HR-form (Curve 1).

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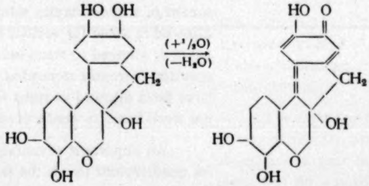
[*] 50 g of onion peel was treated with 100 ml of alcohol and boiled for 2 hours under reflux. The alcoholic solution was poured into 2 liters of water when the quercetin separated out as an orange precipitate. The precipitate was filtered off, dissolved in alcohol and reprecipitated with water. The precipitated quercetin was treated with dilute sulfuric acid on gentle warming. During this state the quercetin separated out as a lemon-yellow precipitate. The precipitate was dried in air. The yield was about 0.3 g of quercetin. This amount of quercetin is sufficient for carrying out about 200 determinations of tin. The commercial preparation of quercetin at our disposal did not give the reaction described with tin.

The results given in Fig. 1 show that for the photometric determination of tin only the visible part of the spectrum can be used. At wave lengths longer than 420 mμ the molecular HR-form of quercetin absorbs light very weakly, while the complex SnR has a wide absorption band. In the range 420-450 mμ the molar absorption coefficient of the complex $E'_{SnR} = 8400$, which characterizes the high sensitivity of the reaction.

A Study of the Reaction of Quadrivalent Tin with Hematoxylin

According to Tartakovskii's results [3] the compound of quadrivalent tin with hematoxylin is stable in acid media. This permits the determination of tin in the presence of aluminum and iron, the lakes of which are unstable in acid media. When solutions of hematoxylin are allowed to stand in air, oxidation of the hematoxylin with formation of hematein occurs [10, 11].



This process speeds up appreciably in ammoniacal media [10]. In studying complex formation between hematoxylin and quadrivalent tin, it is of primary importance to establish which of the two forms – hematoxylin or hematein – reacts with tin. Experiments were therefore carried ou both with freshly prepared 10^{-3} M aqueous solutions of hematoxylin, and aqueous solutions which had been allowed to stand for about one month.

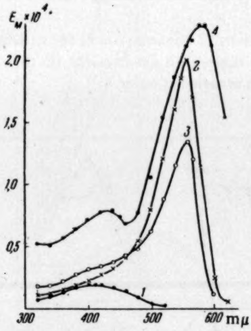


Fig. 2. Absorption spectra of the different forms of hematoxylin: 1) Molecular form (HR); 2) ionic form of hematein; 4) complex with tin (SnR).

Some spectrophotometric characteristics are given in Fig. 2. From this it is evident that in the course of one month, the 10^{-3} M solution of hematoxylin is almost completely oxidized into hematein. The hematoxylin solution as well as the solution of hematein were added to appropriate buffer solutions; in order to study the properties of the complex, the appropriate solutions were mixed so that the total tin concentration was $2.5 \cdot 10^{-5}$, and that of the reagent $5 \cdot 10^{-5}$. 1 ml of a 0.5% freshly prepared solution of gelatin (was added as a stabilizer) per 10 ml of the total volume of solution.

The effect of the pH on the optical density of the solutions is manifested as follows. Free hematoxylin and hematein absorb light weakly at pH < 8. At pH about 8 the color of the solutions increases sharply; at the same time the irreversible oxidation of the reagent is accelerated. Formation of a complex with tin starts in acid media, under these conditions, however, the optical density of the solutions is strongly dependent on the acidity. Formation of a colored complex almost ceases at pH $\geq$ 2. On increasing the pH further the optical density does not change appreciably. Only at a pH of 9 is there observed a breakdown of the complex with the same effect as that described above for the free reagent. The optimum pH values for photometric determinations are pH 2-6 (see Fig. 6 also).

Some of the spectrophotometric characteristics are shown in Fig. 2. Hematoxylin at a pH of 3 (Curve 1) weakly absorbs light in the short-wave part of the spectrum. The absorption spectra of the ionic forms (R^-) of hematoxylin (Curve 2), and of hematein (Curve 3), measured at a pH of 8, are similar to the absorption spectrum of the complex SnR with hematein, this corresponds with the relationship normally observed. The SnR complex has one weaker band at 420 m μ; the absorption here is stronger than for the HR- and R- forms of the reagents. For photometric determination it is best to use the optical density at 590 mμ, where the HR-form of the reagent hardly absorbs light at all, while the complex SnR is characterized by a very strong absorption band. At pH < 6, the ionic form of the reagent is hardly formed at all, and, accordingly, the indicator properties of the reagent have no effect.

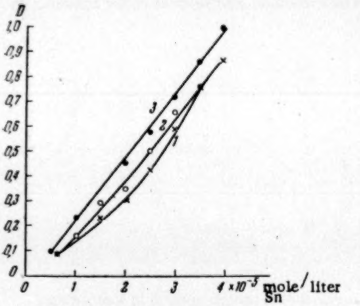


Fig. 3. Relation between the light absorption of solutions of the complex compound of tin with hematoxylin, and tin concentration:
1) with a freshly prepared solution of hematoxylin; 2) with a solution of hematoxylin allowed to stand for 6 days; 3) with a solution which has stood for 2 weeks.

Time during which the solution is allowed to stand does not have a marked qualitative effect on the determination; nevertheless, this time must be taken into account when calibration curves are constructed. In Fig. 3. are shown curves used for the photometric determination of tin by means of a hematoxylin solution, the latter having been allowed to stand for various times before use. When the reagent is allowed to stand beforehand, the sensitivity of the reaction increases somewhat. Solutions of the reagent which have been allowed to stand for two weeks (or more) prior to use were found to conform more closely to Beer's law.

An important advantage of hematoxylin as a reagent for quadrivalent tin, is the fact that neither antimony, or iron form colored complexes with hematoxylin at a pH of 2-3. This fact considerably simplifies the determination of tin.

A Study of the Reaction of Quadrivalent Tin with Stilbazo

According to the results of Kuznetsov et al [6],stilbazo in a weakly acid medium reacts with quadrivalent tin to form a compound with an orange-red color.

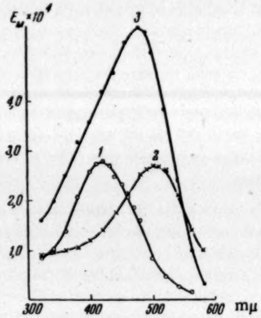


Fig. 4. Absorption spectra of the various forms of stilbazo:
1) The molecular form of stilbazo (HR); 2) the ionic form (R-); 3) the complex with quadrivalent tin (SnR).

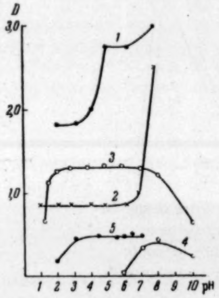


Fig. 5. Effect of pH on complex formation in the system Sn(IV)—organic reagent.
1) The relation between the optical density of solutions of complex of tin and stilbazo,and the pH; 2) solution of stilbazo; 3)solution of the complex of tin with hematoxylin; 4)solution of hematoxylin; 5)solution of the complex of tin with quercetin.

The stock solutions we used were a 10^{-3} M solution of $SnCl_4$ in 1 M hydrochloric acid, and a 10^{-3} M aqueous solution of stilbazo obtained from IREA. *

In Fig. 4 are given the absorption spectra of the HR-, R-, and SnR-forms of stilbazo. Using the isomolar series method, it was established that the composition of the compound formed between quadrivalent tin and stilbazo corresponds to a ratio of the components tin: stilbazo = 1:2. The maximum on the curves is clearly defined, this indicates that the complex is stable.

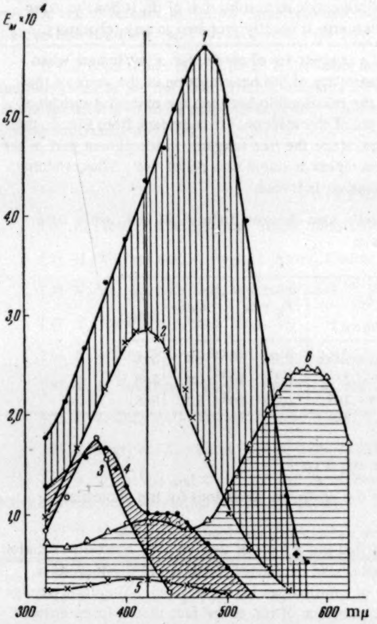


Fig. 6. Absorption spectra of the complex compounds of tin with various OH-containing reagents:
1) The complex of tin with stilbazo; 2) stilbazo; 3) quercetin; 4) complex of tin with quercetin; 5) hematoxylin; 6) the complex of tin with hematoxylin.

Results for the effect of the pH on the light absorption of solutions of the complex compound of tin with stilbazo, and of free stilbazo are given in Fig. 5, for $\lambda_{Eff.}$ = 496 mμ. Formation of a complex compound of tin with stilbazo reaches a maximum at pH 5-7. Stilbazo reagent at a pH of about 6 changes into an ionic R- form which is red in color.

It is clear from Fig. 6 that the indicator properties of stilbazo are a serious hindrance to the use of this reagent in photometry. Qualitative detection of tin is possible within the limits pH 2-6, particularly at a pH of about 6. Nevertheless, in contrast to quercetin and hematoxylin, here small pH variations always show an appreciable effect on the optical density of the solutions. In addition, the intrinsic color of the reagent is signficant, since even even at the optimum pH of about 6, the optical density of a solution of the complex is only twice the optical density of the free reagent (at $\lambda_{Eff.}$ = 440-460 mμ).

Comparison of the Reagents

Of the reagents considered above the most sensitive are quercetin, hematoxylin (oxidized form) and stilbazo. In order to compare these reagents we compared the absorption spectra of the HR- and SnR forms, as shown in Fig. 6. All results are given in E units so that it is possible to compare the reagents independently of the concentration conditions.

The most characteristic criterion is the integral difference between the light absorption of the colored complex SnR and free dye HR; this difference corresponds to the area bounded by the absorption spectrum curves of HR and SnR. In Fig. 6 these characteristic areas are shaded with vertical lines for stilbazo, by horizontal lines for hematoxylin, and by slanting lines for quercetin. By using millimeter tracing paper or by weighing out the pieces of paper cut out in accordance with the areas in Fig. 5., it is possible to compare the absolute and relative differences of the light absorption of the HR- and SnR- forms of the various reagents. The common vertical line separates the visible part of the spectrum. The results given in Fig. 6 show that of the reagents considered, stilbazo is the most sensitive for the qualitative detection of tin.

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*The reagent issued by "Soyuzreaktivsbyt" contains an impurity which completely distorts the reaction with quadrivalent tin,. The reaction for tin can only be carried out after purification of the reagent [12].

During the detection of tin by means of this reagent it is essential (and posible) not to use excess stilbazo, otherwise its own light absorption may complicate observations, and any conclusions which may be drawn. During the photometric determination of tin it is essential to use excess reagent, accordingly its own light absorption will become a serious hindrance. It is also important to point out that in the case of stilbazo, the color of the reagent itself is superimposed on the color of the complex in all parts of the spectrum.

Hematoxylin is a somewhat less sensitive reagent. The integral difference in the light absorptions of the HR- and SnR-forms of the reagent is approximately half that for stilbazo. Nevertheless, from the point of view of quantitative photometric determination, hematoxylin has important advantages, since the light absortion of the reagent itself, is insignificant in comparison with the light absorption of the complex. In the region $\lambda >$ $> m\mu$, the free reagent hardly absorbs light at all.

Quercetin is even less sensitive, nevertheless, for the photometric determination of tin it has the same advantages as hematoxylin. It is essential to point out that quercetin is readily prepared in any laboratory.

It was pointed out above that the indicator properties of a reagent are of particular significance when making a choice of reagent, particularly when there is the possibility of the superposition of the color of the R-form on the color of the complex SnR. In Fig. 5 is shown the relationship between the optical densities of the free reagents, and also of their complex with tin, and the pH of the solution. It is evident from Fig. 5. that the relationship under discussion is most favorable for quercetin, since the free reagent, in the chosen part of the spectrum, in general, does not absorb light. The color of the complex is stable at a pH of 3-6. Thus, random changes in pH of the test solutions have the least effect when quercetin is used.

The color of the complex compound of tin and hematoxylin also changes little at pH 2-6, while superposition of the color of excess reagent can only occur at pH > 6.

Reagent	λ_{max}	E_k (complex)	E_r (reagent)	$E_k - E_r$	$E_k : E_r$	pH range
Quercetin	450	$0.84 \cdot 10^4$	Does not absorb	$0.84 \cdot 10^4$	∞	3-6
Hematoxylin	580	$2.28 \cdot 10^4$	" " "	$2.28 \cdot 10^4$	∞	3-6
Stilbazo	500	$5.00 \cdot 10^4$	$8.7 \cdot 10^3$	$4.13 \cdot 10^4$	5.6	5-6

Conditions for the Photometric Determination of Tin

On the basis of the results obtained, it is possible to give the optimum conditions for the photometric determination of tin by means of the reagents tested.

Determination of tin by means of quercetin should be carried out a a pH of 3-5 in 50% alcoholic solution. Measurements of the light absorption of the tin-quercetin complex can be carried out in a FM-1 photometer using light-filter 7 ($\lambda_{Eff.}$ 465 $m\mu$). 1-15 γ of tin in 15 ml of solution can be determined. The disadvantage of quercetin, like most other reagents for the photometric determination of tin, is the fact that it forms colored compounds with a number of elements, including antimony and iron. These two elements are the ones which accompany tin most often. A study of the effect of various complexing agents as masking agents, such as tartrates, oxalates, fluorides, and Complexon III did not yield the desired results. All these materials form colorless complex compounds with tin, thereby weakening the color of the solutions of the complex of tin with quercetin. For antimony contents equivalent to those of tin, determination of tin by means of quercetin is possible, since antimony under these conditions does not give an appreciable color with quercetin. The effect of iron during the photometric determination of tin with quercetin can be elmiminated by reduing iron to the divalent state by means of thiourea.

Photometric determination of tin with hematoxylin should be carried out at pH 3-5. 5-10 γ of tin in 15 ml of solution can be determined. The concentration of the hematoxylin solution used should be 0.06%. 0.5 ml of this solution is taken for one determination. Light absorption is measured on a FM-1 photometer fitted with a No. 4 light-filter ($\lambda_{Eff.} = 574\ m\mu$).

Tin is determined photometrically with stilbazo at a pH of 5. The pH of both the standard and test solutions must be strictly controlled. The concentration of the stilbazo reagent used is 0.05%. 0.5 ml of reagent solution is taken for one determination. 5-10 γ of tin can be determined in 15 ml of solution. Interference from iron can be suppressed by addition of a saturated solution of thiourea to the solution. Light absorption is measured on a FM-1 photometer using a No. 6 light-filter ($\lambda_{\text{Eff.}} = 496$ mμ).

SUMMARY

A comparative spectrophotometric study has been made of some hydroxyanthraquinones, quercetin, hematoxylin, and stilbazo as possible reagents for quadrivalent tin. The criteria used for making a choice of a suitable reagent was the integral difference between the light absorption of the colored complex SnR and the free dye HR, and also the difference in the pH range between complete formation of the colored complex and the transition of the dye into the ionic form R^-.

It has been shown that stilbazo is the most sensitive reagent for the qualitative detection of tin. Quercetin and hematoxylin are the most suitable reagents for the photometric determination of tin. Comparative data on the sensitivity of these reagents is given, together with the optimum pH conditions for carrying out the reactions for quadrivalent tin.

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HIGH-VOLTAGE ELECTRODIALYSIS

COMMUNICATION 2. THE REMOVAL OF IMPURITIES FROM METASTANNIC ACID*

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It was shown in a previous article [1] that during the electrodialysis of silicic acid, Fe, Cu, Pb, and Cd present as impurities to the extent of 10^{-2} - 10^{-3}% in the original material can be removed quantitatively down to the limits of the sensitivity of the spectrographic method (about 10^{-4}%). This result was in agreement with results published previously by V. L. Kargin and M. A. Matveeva [2].

It was of interest to examine the possibility of carrying out quantitative separation of metals present as impurities in metastannic acid, gels of which exhibit high absorption properties and trap most cations during precipitation. We carried out tests on the electrodialysis of metastannic acid containing the impurities indicated above to the extent of 10^{-1}%. In addition we carried out tests on the separation of unweighable amounts (traces) of active lead ThB and also of active antimony Sb^{125} in order to assess the possibility of removing impurities under these conditions.

TABLE 1

Spectrographic Analysis of Metastannic Acid Precipitates after Dialysis

Initial content of Fe, Cu, Pb, and Cd (before dialysis) $1 \cdot 10^{-1}$ %

Metal	Method of Preparation	
	First method	Second method
Fe	$1 \cdot 10^{-1}$	$2 \cdot 10^{-2}$
Cu	$0.74 \cdot 10^{-1}$	$8 \cdot 10^{-2}$
Pb	$1 \cdot 10^{-1}$	$8 \cdot 10^{-2}$
Cd	$1 \cdot 10^{-1}$	$5 \cdot 10^{-2}$

*Treatment of metallic tin with concentrated HNO_3.

**Precipitation of Sn^{IV} hydroxide with ammonia.

When dealing with weighable amounts of impurities, preparation of the samples of metastannic acid was carried out as follows.

First Method

An aliquot of metallic tin (usually 1 g) was dissolved in a few ml of concentrated HNO_3 containing 1 mg each of the impurities indicated (in terms of the metal) in the form of their nitrates.

Second Method

An aliquot of metallic tin (1 g) was dissolved in concentrated HCl, and the divalent tin oxidized by means of iodine solution; to the solution thus obtained, 1 mg each of the impurities indicated above were added (in the form of nitrates), and the hydroxides precipitated by means of concentrated ammonia. In both cases the suspension of metastannic acid formed was freed from excess electrolytes by means of centrifuging or filtration on a glass filter under suction, and consequent washing of the precipitate with hot water.

When the first method was used more dense precipitates were obtained, while when the second method was used the precipitates were more friable and amorphous. It might be expected that separation of impurities from precipitates obtained by the second method would be more complete [1].

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*For communication 1, see [1].

The precipitates prepared were quantitatively transferred to the middle cell of a three-cell analyzer with cellophane membranes. Electrodialysis was carried out with cellophane membranes in an "ionic current" [2]; for this purpose the cathode cell was filled with HNO_3 solution win an initial concentration of 10^{-1} to 10^{-3} N, while the anode cell and the middle cell were filled with twice distilled water.

The experiments were continued until a minimum current was established (5-7μa), and, accordingly, a maximum voltage (2000 volt). Periodically, the solutions from the anode and cathode cells were poured into separate flasks and the impurities separated analyzed photometrically and polarographically. The contents of the impurities in the metastannic acid before and after dialysis were determined spectrographically. The results of the electrodialysis are given in Table 1.

As is evident from Table 1, removal of impurities of Fe, Cu, Pb, and Cd proceeds better from the gel of metastannic acid prepared by the second method, where the gels have a more amorphous structure and have more discrete particles than in the case of the gels obtained by means of the first method.

TABLE 2

Distribution of Activity (ThB) After Electrodialysis of Metastannic Acid Activity of the Solution Added to the Precipitate Amounted to 10,888 impulses/minute

Test solution	Volume of solution	Activity of 1 ml of solution, impulses/minute	Activity (%) of all the solution, impulses/minute	As % of the activity introduced
From the cathode cell	3	88	264	2.43
From the anode cell	10	7	70	0.64
Filtrate and wash liquor	5	20	100	0.72
After treating the ash of the anode membrane	1	58	58	0.53
After treating the ash of the cathode membrane	3	504	1512	14
Total removed from the precipitate			–	18.3
Held by the precipitate				81.7%

Nevertheless, the impurities are not removed quantitatively, and are removed to varying extents from the amorphous precipitates. The percentage content of iron is lowered one order, while the percentage content of the remaining metals (Cu, Pb, and Cd) are lowered to less than one half of an order.

As for precipitates of metastannic acid prepared by the first method, the impurities indicated are hardly removed at all in these cases. Thus, the possibility of effecting a quantitative removal of metal impurities from precipitates dispersed in water, depends, on the one hand, on the chemical nature of the dispersed material and the impurities themselves, and also, apparently, on the nature of the bond between the impurity and the particles of the dialyzed material [1].

During work with trace amounts of impurity, an aliquot of tin sulfate (0.3616 g) was dissolved in 5 ml of HCl. To this solution was added 1 ml of a soltuion of the nitrate of active lead ThB (without a carrier) *; after oxidation of divalent tin with iodine solution, the quadrivalent tin was precipitated with concentrated ammonia.

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*We should like to thank G. N. Bilimovich for preparing the ThB used. The absolute amount of ThB introduced into the metastannic acid corresponded to 10^{-17} g. atom.

The solution, plus the deposited precipitate of tin was heated to the boil, and, after removing the mother liquor, the precipitate was centrifuged and washed three times with water. Filtrate and wash liquors were combined in one flask and the whole evaporated to a small accurately measured volume; this volume of solution was used for determining the activity of the material not trapped by the metastannic acid.

The precipitates were subjected to electrodialysis in an "ion current," the cathode cell being filled with a solution of HNO_3 with an initial concentration of 0.01 N; electrodialysis was carried on until a minimum current value was established (5-7 μa), and, accordingly, a maximum voltage.

During the electrodialysis process the solutions were poured out of the electrode cells into separate flasks and the cells then filled up again : the anode cell with twice-distilled water, and the cathode cell with a solution of 0.001 N HNO_3, while towards the end of the test it was filled with twice-distilled water.

All the solutions which were poured out of the electrode cells were evaporated on a water bath to small, accurately known volumes which were then used for determining the activity contained in them.

The ash of the anode and cathode membranes was treated with a small amount of concentrated nitric acid, and the solutions obtained used also for activity measurements.

The distribution of activity after electrodialysis in the anode and cathode solutions, and also in the ash of the membranes (anode and cathode is given in Table 2. It is clear from this table that unweighable amounts of impurities are hardly removed at all from precipitates of metatannic acid.

Similar results were also obtained on introducing activity antimony into metastannic acid precipitates.

Active antimony was introduced into a solution of $SnCl_2$ obtained by dissolving 1 mg of metallic tin in concentrated HCl, with subsequent addition of hydrogen peroxide, and precipitation of metastannic acid by means of concentrated ammonia solution. Excess of the electrolytes introduced were removed by electrodialysis. The precipitate of metastannic acid purified from excess electrolytes was subjected to electrodialysis in an ion current, for which purpose 0.1 N HCl in 2 ml portions was added four times into the cathode cell.

Solutions from the anode and cathode cells were periodically poured out and replaced by twice-distilled water; the collected solutions were concentrated by evaporation and their specific activity in impulses / minute determined. In the course of this work it was established that antimony hardly passes at all into the side cells as a result of electrodialysis. It was absent in the solution above the precipitate of metastannic acid in the middle cell and in the membrane material (the membranes were ashed before carrying aout activity measurements).

On the basis of the work carried out it can be concluded that trace amounts of lead and antimony cannot be removed at all from metastannic acid by means of electrodialysis.

SUMMARY

By subjecting metastannic acid with an initial concentration of Fe, Cu, Pb, and Cd of 10^{-1}% to electrodialysis, the content of these impurities can be reduced by 0.5 - 1 order. Traces of ThB and Sb^{125} cannot be removed from metastannic acid by means of electrodialysis.

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CHROMATOGRAPHIC SEPARATION OF AROMATIC CARBONYL COMPOUNDS

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The chromatographic method which has been used for separating the most diverse classes of compounds (sugars, amines, acids, amino- and ketoacids, carbohydrates alcohols, phenols, hydrocarbons, aldehydes, ketones, etc) and which has been used on a wide scale in recent years, makes it possible to solve a number of difficult analytical problems which often cannot be solved by ordinary chemical methods.

There are two paper chromatographic methods which differ from each other in principle, these are: adsorption and partition chromatography. Resolution of a mixture during adsorption chromatography is based on differences in the absorbability of the components of the mixtures on the absorbent (cellulose, acetylcellulose,etc), and depends both on the properties of the sorbent and on the choice of a suitable solvent. Separation of mixtures by means of partition chromatography is determined by differences in the partition coefficients of the components between two immiscible phases, one of which is located in the pores of the sorbent—the stationary phase —, while the second is the mobile phase. Hydrophilic materials (silica gel, cellulose, and starch) are widely used as the aqueous adsorbent. Various organic solvents usually serve as the mobile phase. The efficiency of partition chromatography is determined by the correct choice of the mobile and stationary phases ensuring the maximum possible difference in the partition coefficients of the mixture between the two phases.

Our problem was to develop a technique for the chromatographic separation of a complex mixture of aromatic carbonyl compounds formed during the oxidation of diphenylethane (benzyl, desoxybenzoin, benzoin, benzaldehyde, and phenylacetaldehyde).

There is a large amount of published work on the chromatographic separation of carbonyl compounds of various classes. There is, however, as yet, no published information on the separation of the mixture we are interested in.

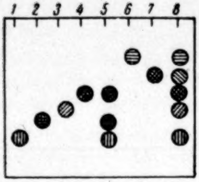
Some of the articles give some information on the possibility of separating carbonyl compounds without having to resort to making other compounds from them first [1-2], nevertheless, in most cases, derivatives of the carbonyl compounds are used. Some aldehydes and ketones can be separated in the form of their Girard derivatives [3]. These derivatives are readily soluble in water and in organic solvents. In this case the system water (adsorbed by cellulose) — organic solvent is used. Using this method, for example, 5-hydroxy-methyl-2-furfuraldehyde, 2-furfuraldehyde, and 5-methyl-2-furfuraldehyde ; salicylaldehyde, and 4-hydroxy-3-methoxy-benzaldehyde [4] have been separated.

The most widely used and the most convenient method is the separation of carbonyl compounds as their 2,4-dinitrophenylhydrazones. Both adsorption and partition chromatographic techniques can be adopted when these derivatives are used.

Separation of the 2,4-dinitrophenylhydrazones can only be achieved with difficulty on normal chromatographic paper [5] because of the hydrophilic character of cellulose. In order to get good results it is necessary to give the paper a hydrophobic character, this is carried out by esterifying the cellulose with acid anhydrides (acetic, benzoic, butyric, tartaric anhydrides, etc) [6-7].

The lower aliphatic aldehydes and ketones can also be separated on paper impregnated with sodium silicate [8].

The system most often used in the practice of partition chromatography is the system water-organic solvent, nevertheless, for the separation of carbonyl compounds such sustems have a very limited application; they are used only for the separation of hydroxyaldehydes and hydroxyketones, and the 2,4-dinitrophenylhydrazones of keto acids [9-14]. Separation of the 2,4-dinitrophenylhydrazones of aliphatic aldehydes and ketones is achieved by partition between two organic solvents [15-21]. In attempting to use partition chromatography for our system we tried out almost all the solvents suggested in the literature (petroleum ether, CCl_4, benzene, alcohol, ethyl ether, $CHCl_3$, dimethylformamide, heptane, etc.). In most cases, after developing the chromatograms, continuous bands, with only a small intensification of color on individual parts, were obtained on the paper. When certain systems were used (diethyl ether and petroleum ether) diffuse spots were obtained, nevertheless, even in these cases, despite differences in the R_f values, we were unable to separate the hydrazones. Attempts to use adsorption chromatography on acetylated paper also proved unsuccessful — compact zones were obtained, but without sufficient differences in the R_f values.



A chromatogram of the 2,4-dinitrophenylhydrazones of the aromatic carbonyl compounds, and of their mixture:
1) Benzoin; 2) benzaldehyde; 3) phenylacetaldehyde; 4) benzyl; 5) a mixture of benzoin, benzaldehyde, and benzyl; 6) 2,4-dinitrophenylhydrazine; 7) desoxybenzoin; 8) a mixture of benzoin, phenylacetaldehyde, benzyl, desoxybenzoin, and 2,4-dinitrophenylhydrazine.

A clear cut separation of the hydrazones of the aromatic carbonyl compounds was only obtained on using a combination of both chromatographic methods. Of the large number of systems tested the best one proved to be a system consisting of acetylated paper (adsorbent) impregnated with n-octyl alcohol (stationary phase) — and a mixture of hexane, toluene, and acetic acid in the proportions of 6:1:3 by volume (mobile phase).

The adsorption properties of acetylcellulose are of considerable importance for obtaining good results. In order to get uniform acetylation of the paper according to a method described previously, we used a thin spiral of teflon on which was wound a sheet of paper. Adoption of this technique prevented the sheets from sticking and the paper obtained was uniform along its whole surface. When the acetylating mixture contained even the smallest amounts of undissolved sulfuric acid, which was used as the esterification catalyst, the paper obtained was not suitable for the work, since it was brittle and unstable. Accordingly, it is essential to remove the layer of H_2SO_4 as carefully as possible from the acetylating mixture.

In order to develop this technique of chormatographic separation, synthetic mixtures were made up from carefully purified carbonyl compounds. Benzyl and benzoin (commercial) were recrystallized twice from ethanol and had melting points of 95° for benzyl and 133° for benzoin (published data 95° and 133.7°, respectively).

Phenylacetaldehyde and benzaldehyde (commercial) were distilled, the fraction boiling at 193-194° being chosen for phenylacetaldehyde and that boiling at 178-179° for benzaldehyde. The boiling points of the pure materials according to published data are 194° and 179.5°. Desoxybenzoin was prepared by the reduction of benzoin. The temperature of the material thus prepared agreed with the published value (59°).

Dinitrophenylhydrazones were prepared by the interaction of 2,4-dinitrophenylhydrazine with the corresponding compound in a weakly acid methanol solution [22]. This solution was chromatographed immediately without any procedures involving deposition of a precipitate. This speeds up and simplifies the analysis considerably. Excess 2,4-dinitrophenylhydrazine as we have shown, does not interfere with the chromatographic separation of the hydrazones, since on developing the chromatograms, this material gives its own characteristic zone which does not overlap the zones of any of the hydrazones (it is higher than all the other zones). The solution containing the 2,4-dinitrophenylhydrazones was placed on a piece of acetylated paper 120-300 mm, soaked beforehand with a 5% solution of n-octyl alcohol in CH_3OH and dried in air for 30-45 minutes. Careful drying is essential for complete removal of CH_3OH, in whose presence the zones obtained for 2,4-dinitrophenylhydrazones are less compact. The paper was then placed in a cylinder with a volume of about 2 liter, on the bottom of which was poured

30-40 ml of a mixture of hexane, toluene, and acetic acid. Under these conditions, a complete run could be carried out in 4-4.5 hours. A typical chromatogram for a mixture of the 2,4-dinitrophenylhydrazones of benzyl, desoxybenzoin, benzoin, benzaldehyde, and phenylacetaldehyde, obtained by this technique, is shown in the diagram. The yellow spots of the hydrazones, after spraying with alcoholic alkali, acquire colors which are characteristic of each carbonyl compound, the colors ranging from yellow-brown to lilac (Table 1).

TABLE 1

Test compound	R_f	Color of the spot after spraying with alcoholic alkali
2,4-Dinitrophenylhydrazine	0.76	Dirty-black
Hydrazones		
Benzoin	0.34	Yellow-brown
Benzaldehyde	0.45	Brown
Phenylacetaldehyde	0.53	Dark-brown
Benzyl	0.58	Lilac
Desoxybenzoin	0.67	Dark-brown

TABLE 2

Test compound	Initial concentration	Amount of solution taken, ml		Contraction found
		for the analysis	for the chromatogram	
Benzaldehyde	5,48 mg in 10 ml	0,3	0,4	5,94 mg in 10 ml
Benzyl	4,52 mg in 10ml	0,1	0,4	4,5 mg in 10 ml
Benzoin	4,8 mg in 10 ml	0,1	0,4	4, mg in 10 ml
Desoxybenzoin	2 mg in 10 ml	0,1	0,4	1,96mg in 10 ml

Table 1 also contains the calculated R_f values for the corresponding hydrazones. The R_f values were determined from the rates at which the solvent front and the zones moved.

These results show that it is possible to separate and identify all the carbonyl compounds formed during the oxidation of diphenylethane by a simple and convenient method.

The method developed can also be used for the separate quantitative determination of the carbonyl compounds indicated. The amount of hydrazone which can be determined is limited on the one hand, by the sensitivity of the method (10^{-7} M), and on the other hand by the solubility of the hydrazone in methanol ($2 \cdot 10^{-5}$ M in 2 ml of CH_3OH in the case of benzaldehyde, which gives the less soluble hydrazone). Accordingly, about 100 γ of the mixture of hydrazones was placed on the paper in the form of 5-8 mm wide bands. After the chromatograms had been allowed to run, each band was extracted separately with alcoholic alkali and the optical density of the solutions thus obtained measured on a FÉK-M photoelectric colorimeter. A curve showing the relation between the optical density of the solution, and the concentration of the hydrazone of the corresponding carbonyl compound, was constructed beforehand.

Table 2 illustrates the results obtained during the quantitative chromatographic separation of a synthetic mixture of benzyl, benzoin, and benzaldehyde.

In conclusion the author would like to thank N. M. Emanuel and E. A. Blyumberg for their valuable advice during the course of this work.

SUMMARY

A chromatographic method has been developed for the separation and quantitative determination of aromatic carbonyl compounds as their 2,4-dinitrophenylhydrazones. The determination is carried out on acetylated paper impregnated with n-octyl alcohol. The mobile solvent is a mixture of hexane, toluene, and acetic acid (6:1:3 by volume). The method has been used for separating a mixture of benzaldehyde, phenylacetaldehyde, benzoin, desoxybenzoin, and benzyl.

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POLAROGRAPHIC ANALYSIS OF THE LIQUID PRODUCTS OBTAINED DURING THE NITRATION OF ALKANES WITH NITROGEN DIOXIDE

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Vapor-phase nitration of alkanes (C_1-C_3) by means of nitrogen dioxide leads to the formation of a mixture of products, the quantitative analysis of which presents considerable difficulties. In such mixtures, in various experiments, the following compounds have been shown to occur: nitroparaffins, alkylnitrites, alkylnitrates, aldehydes, alcohols, alkanes, alkenes, carbon monoxide and dioxide, nitrogen oxides, and water [1-5]. Of these, nitrogen oxides, carbon oxides, and the hydrocarbons can be determined by the usual chemical or chromatographic methods. For this purpose, it is only necessary to shake the mixture with water, to remove from it the liquid reaction products (nitroparaffins, alkylnitrites and alkylnitrates, aldehydes, and alcohols) and the residue of NO_2. Analysis of the liquid products in each others presence cannot be, as yet, regarded as developed sufficiently, and this strongly impedes the development of studies of the nitration reaction.

Analysis of Liquid Nitration Products in the Absence of NO_2

An examination of the results given in Table 1 leads to the conclusion that the polarographic technique would appear to be a promising method for the analysis of such mixtures.

TABLE 1

Half-Wave Potentials ($\pi_{1/2}$) Relative to the Saturated Calomel Electrode (S.C.E.)

Compound	Half-wave potential, volt		
	Acid medium	Neutral medium (pH 7)	Alkaline medium (pH 12)
RNO_2[*] [1]	− 0.6	−0.85	− 1.0
RONO [2]	hydrolyzes	−	− 0.65
$RONO_2$[3]	−	−0.70	− 0.65
HCHO [4]	−	−1.41	− 1.66
CH_3CHO [5]	−	−1.63	− 1.89

[*] $\pi_{1/2}$ does not depend on R.

In alkaline media the half-wave potentials of each material given in Table 1 differ sufficiently from each other in value to ensure their separate polarographic determination. Only the alkylnitrites and alkylnitrates are exceptions. Nevertheless, even in these cases, a combination of the spectrophotometric determination of alkylnitrite, with the polarographic determination of total alkylnitrites and alkylnitrates, makes it possible to determine each of them. [6].

The wave height for the reduction of alkylnitrites a and alkylnitrates is almost independent of the pH of the medium in the range 8 to 13 (Fig. 1).[*] In the same way the wave height of acetaldehyde also remains unchanged for pH changes from 10.5 to 12.5. The reduction wave of formaldehyde has a clearly defined maximum at pH 12.5, when the pH is changed from 7 to 13. Accordingly, formaldehyde in an alkaline medium must be determined at an accurately controlled pH corresponding to the point at which the maximum wave height is obtained. Finally, in the case of the nitroparaffins the wave height is a maximum and is constant at pH 2-7.

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[*] Polarograms were taken on a "Geolrazvedka" polarograph, 1954 model. The capillary characteristics were $m^{2/3} t^{1/6}$ = =2.86 mg$^{2/3}$ sec$^{1/2}$. 1 mm wave-height corresponds to $4.4 \cdot 10^{-9}$ amp. at maximum sensitivity. pH was measured on a LP-5 potentiometer using a glass electrode. Corrections for the readings of the glass electrode in the alkaline region were not made here or below.

Thus, it can be suggested that an analysis of a mixture of the liquid nitration products of alkanes should be carried out both in alkaline and in neutral solutions; in the first medium, alkylnitrites, alkylnitrates, and aldehydes are determined, while in the second the nitroparaffins are determined. It was found, however, that the polarographic analysis of such a mixture is complicated by the capacity of the nitroparaffins to give two reduction waves not one. Petru [7] was the first to observe this phenomenon when taking polarograms of nitroethane in a Britton-Robinson buffer (pH- 1.81-11.98). Under these conditions one wave was obtained with $\pi_{1/2}$ = -0.7 volt, and a second wave (half the size) with $\pi_{1/2}$ = -1.5 volt. We found that during the polarographic reduction of nitromethane in a solution of LiCl (pH 5-6) only one wave with π = -0.85 volt was always obtained. In solutions of NaH_2PO_4 - NaOH or NaH_2PO_4 LiOH (pH 5-7), however, sometimes, there appeared two waves with $\pi_{1/2}$ = -0.85 volt and with $\pi_{1/2}$ = -1.6 to—1.8 volts, respectively. In alkaline solutions (0.2 M LiOH) of nitromethane, the second wave also appears in those cases where the solution is kept for some time before taking polarograms. Under these conditions, the higher the nitromethane concentration, the sooner the second wave appears. The height of the first wave for nitromethane is independent of the time for which the solution is kept before taking polarograms, accordingly, any quantitative determinations of the nitroparaffins should be based only on the height of the first wave. However, under these conditions, determination of formaldehyde becomes difficult, because the height of the second wave of the nitroparaffin which coincides with respect to its reduction potential with the reduction potential of formaldehyde, is subjected to sharp changes which occur for some reasons hitherto unknown.

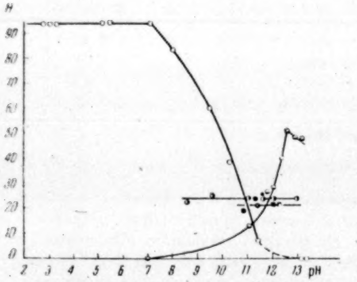

Fig. 1. Relation between wave-height and pH in unbuffered solutions (s = 1:100). o) 0.001 M solution of CH_3NO_2 (determined for a 0.00031 M solution) at 20°, supporting electrolyte 0.1 M LiOH + HNO_2; O) 0.005 M HCHO solution (determined for 0.0077 M solution) at 25°, supporting electrolyte 0.1 M LiOH+ + HNO_2; O) 0.001 M solution of CH_3CHO (determined for 0.01 M solution), 25°, supporting electrolyte 0.1 M LiOH + 0.1 M LiCl; O) 0.001 M solution of C_2H_5ONO (determined for 0.0038-0.0058 M solution), 25°, supporting electrolyte 0.1 M LiOH + LiCl.

To avoid the phenomenon of two waves for nitroparaffins, at least for long enough to take polarograms, it is sufficient to store the solutions at 0°.

All the same, during the polarographic analysis of a mixture of aqueous solutions of nitromethane, ethylnitrite, acetaldehyde, and formaldehyde, the results obtained were not satisfactory. The negative error obtained during the quantitative determination of alkylnitrites and aldehydes was very large, particularly in the case of the aldehydes (up to 50%). It was thought that one of the sources of error is the instability of some of the test materials in neutral or alkaline solutions at room temperature.

In checking this last assumption it was found that solutions of nitromethane, acetaldehyde, and formaldehyde (0.001- 0.03 M solutions) in water were stable for at least several months, while when dissolved in 0.1 N LiCl and in a neutral buffer of 0.2 M NaOH + 0.2 M NaH_2PO_4 they were stable for not less than a few hours. In a solution of 0.2 M LiOH the wave height for nitromethane (0.015 M) with $\pi_{1/2}$ = - 0.85 volt does not change in the course of 15 hours, while the wave height for formaldehyde (0.01 M) does not change in the course of 48 hours; the wave height for acetaldehyde, however, changes by 10% in 1.5 hours. Ethylnitrite hydrolyzes slowly in neutral solutions (H_2O, 0.1 M LiCl), nevertheless, its 0.005 M solution in 0.2 M LiOH is stable for one hour. Thus, the negative error obtained in the results for the analysis of a mixture at room temperature, cannot be explained by any interaction between the test materials and the components of the supporting electrolyte.

Another possible reason for the negative error is the interaction of these materials with each other in solution at room temperature; for example, it is well known that nitroparaffins react fairly readily with aldehydes to form nitroalcohols. In this connection therefore, solutions of binary mixtures of nitromethane and formaldehyde in 0.2 M LiOH were examined polarographically at room temperature, and the wave height for formaldehyde measured after certain time intervals. At 20° there is a fairly rapid decrease in formaldehyde concentration (Table 2) which can naturally be ascribed to its reaction with nitromethane. It was found, however, that this drop in the wave height for formaldehyde in alkaline solution is not accompanied by a drop in the wave-height for nitromethane; this last fact was established by measuring the wave height at $\pi_{1/2} = -0.85$ volt in neutral solutions prepared by mixing alkaline solutions of formaldehyde, stored for a certain time, with 0.2 M NaH_2PO_4 solution. The fact that the wave height for nitromethane remains constant while that of the formaldehyde drops at the same time (when they are present together) may, presumably, be explained on the grounds that not only the shape and potentials of the nitroparaffin and nitroalcohol coincide (this has been observed by Seagers and Elving [8]) but also the height of the reduction wave.

TABLE 2

Change of the Height of the Reduction Wave for Formaldehyde with Time in a Solution which is 0.0006 M with respect to Formaldehyde. 0.002 M with respect to CH_3NO_2 and 0.13 M with respect to LiOH

Temperature °C	Time after solutions have been made, minutes	Wave-height, mm	Sensitivity (s)	Temperature °C	Time after solutions have been made, minutes	Wave-height, mm	Sensitivity (s)
20	0	56	1 : 100	0	0	34,5	1 : 30
20	13	47	1 : 100	0	18	34,5	1 : 30
20	31	38	1 : 100	0	48	35	1 : 30
20	42	35	1 : 100	0	148	27	1 : 30
20	68	27	1 : 100				

It follows from the results given in Table 2, that the reaction between the aldehyde and nitroparaffin can be slowed down appreciably by storing their alkaline solution at 0°.

A General Method for the Analysis of Liquid Products in the Absence of NO_2

On the basis of what has been said above the following experimental procedure can be adopted for the analysis of the products obtained during the vapor phase nitration of alkanes, in the absence of NO_2. Nitration itself was carried out under static conditions, where the initial pressure of alkane did not exceed 200 mg Hg (1.5- 1.7 millimole). At a chosen moment when all the NO_2 had already been transformed, the reaction mixture was withdrawn from the reactor into an evacuated trap cooled with liquid nitrogen. 20 ml of 0.2 M LiOH, or 20 ml of a buffer solution of 0.2 M NaOH + 0.2 M NaH_2PO_4 with a pH of 6-7, was then added to the trap before its contents had frozen; on adding this solution it partially froze on the trap walls during the first moment of addition. As the solution melted the trap was shaken. After the liquid products had dissolved the nitrogen oxide was removed from the trap by gaseous nitrogen at a temperature not greater than 0°. Formaldehyde and acetaldehyde were determined in 0.2 M LiOH at 0°. In calculating the formaldehyde concentration the pH was taken into account, the relation between wave height and pH having been established beforehand. Total alkylnitrites and alkylnitrates[*] — if present[**] — can be determined in this same solution. Total nitroparaffins were determined in a buffer solution of 0.2 M NaOH (or LiOH + 0.2 M NaH_2PO_4) with a pH of 6-7 at 20°. The solution was obtained either by mixing a solution of the phosphate with part of the alkaline solution of the reaction products, prepared for determination of the aldehydes and alkylnitrites, or, by dissolving the reaction products directly in the buffer solution. In the first instance, the solution should be kept at room temperature for 1.5 hours before taking polarograms,

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[*] The alkylnitrites were also determined on a SF-4 spectrophotometer.

[**] We did not find alkylnitrites and alkylnitrates during the thermal nitration of alkanes under the conditions we chose.

polarograms, in order to allow the aci-form of the nitroparaffin to change over completely into the nitro-form which is necessary for polarographic measurements. This analytical variant has been checked on synthetic mixtures and is applicable to the analysis of the liquid products obtained during the nitration of propane and methane under static conditons. In Tables 3 and 4, and in Fig. 2 are shown the analytical results for synthetic mixtures. These mixtures were prepared from aqueous solutions of the components (apart from C_2H_5ONO, which was dissolved in 0.2 M LiOH at 0°).

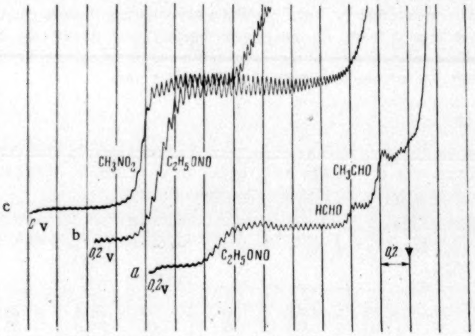

Fig. 2. Polarograms of synthetic mixtures.
a) Ethylnitrite, formaldehyde, and acetaldehyde in 0.2 M LiOH the concentrations of the components were: C_2H_5ONO-0.0063 M, HCHO-0.0120 M, CH_3CHO- 0.0027 M, CH_3NO_2-0.0056 M; s = = 1:200; 0°; pH 12.5; b) 0.0102 M ethylnitrite in a control solution of 0.2 M LiOH; s = 1:200; 0°; pH 12.5; c) nitromethane in a mixture of 1 ml of solution a) and 5 ml of a solution of 0.2 M NaH_2PO_4 : = s = 1:200; 0°; pH 6.3.

TABLE 3

Polarographic Analysis of Synthetic Mixtures in the Absence of NO_2

CH_3CHO m/liter		HCHO, m/ liter		C_2H_5ONO, m/liter		CH_3NO_2, m/ liter	
taken	found	taken	found	taken	found	taken	found
0,00034	0,00029	0,0020	0,0024	0,0055	0,0077	0,0070	0,0065
0,0027	0,0024	0,0120	0,0120	—	0,0018	0,0056	0,0055
0,0027	0,0024	0,0120	0,0120	0,00630	0,00567	0,0056	0,0056

The Analysis of Liquid Nitration Products in the Presence of NO_2

Additional difficulties arise when some of the nitrogen oxide which has not reacted is present in the reaction products. These arise as a result of two factors: 1) the interaction of nitrous acid, formed during the dissolution of nitrogen dioxide in water, with nitroparaffin to form nitrolic acids, and 2) the shift of the reduction potentials of Na^+ and Li^+ toward more negative values in the presence of NO_2^- and NO_3^- anions, which arise as the result of the dissolution of nitrogen dioxide in water; this renders polarographic determination of aldehydes difficult, and, sometimes impossible.

TABLE 4

Effect of the Time for which the Mixtures are Kept on Wave Height (sensitivity (s) 1:200)

Test material and concentration, mole/liter	Electrolyte	Temperature	Time, minutes (*t*) 0	5	33	50	75
			Wave-height, mm				
CH_3CHO (0,0027)	0,2 *M* LiOH	0°	27*	24	21	19	16
HCHO (0,012)	0,2 " "	"	8*	8	8	8	8
C_2H_5ONO (0,00630)	0,2 " "	"	16,2*	14,5	14	14	14
CH_3NO_2 (0,0056)	0,2 *M* NaOH+0,2 *M* NaH_2PO_4 pH 6—7	20°	43*	—	—	—	43

*Calculated on the basis of the wave-height in the one component control solution; the time when the mixture is made up is taken as t = 0.

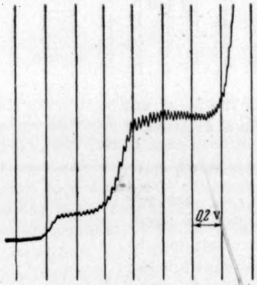

Fig. 3. Polarogram of methylnitrolic acid obtained by dissolving a mixture of the vapors of 0.3 millimole of NO_2 and 0.085 millimole of CH_3NO_2 in 20 ml of 0.2 M LiOH; s = 1:200; 0°; pH 12.4.
The first abscissa at 0.4 volt.

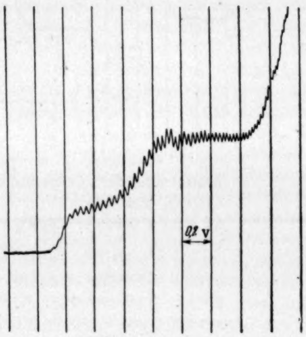

Fig. 4. Polarogram of methylnitrolic acid synthesized by Gatterman's method, and dissolved in 0.2 M LiOH; s = 1:500; 20°; pH 12.5.
First abscissa at 0.2 volt.

Attempts to remove nitrogen dioxide directly from a partially reacted mixture of RH and NO_2 which is to be analyzed, without changing the composition of the remainder, proved unsuccessful. Accordingly, the difficulties indicated had to be overcome by another method.

a) Polarographic Analysis of a Mixture of Nitroparaffin and NO_2. On dissolving a mixture of a nitroparaffin and nitrogen dioxide in a large excess of an aqueous alkaline electrolyte (under the experimental conditions) formation of free nitrous acid cannot be avoided. The latter slowly reacts with the nitroparaffin to form nitrolic acids, which leads to a decrease in the nitroparaffin concentration. We were unable to avoid formation of nitrolic acids by lowering the temperature at which the components were dissolved, or by cutting down the time taken to dissolve the components by mixing (down to one second). In Fig. 3 is shown the polarogram of an alkaline solution obtained by pouring 20 ml of 0.2 M LiOH into a mixture of 0.085 millimole of nitromethane and 0.3 millimole of nitrogen dioxide frozen at -78°. Two reduction waves can be observed on the polarogram, one with $\pi_{1/2} = -0.6$ volt and a second with $\pi_{1/2} = -1.1$ volt.• Similar waves were obtained during the reduction of alkaline (0.2 M LiOH) solutions of methylnitrolic acid synthesized either by Gatterman's method [9] (Fig. 5) or by acidification of a mixture of aqueous solutions of nitromethane and $NaNO_2$ (see Fig. 5). This confirms the formation of a nitrolic acid on dissolving a frozen (-78°) mixture of nitromethane and NO_2 in 0.2 M LiOH, presumably, as the result of the appearance of free acid in various parts of the mixture. In this case, from 10 to 40 % of the original nitromethane is converted into a nitrolic acid.

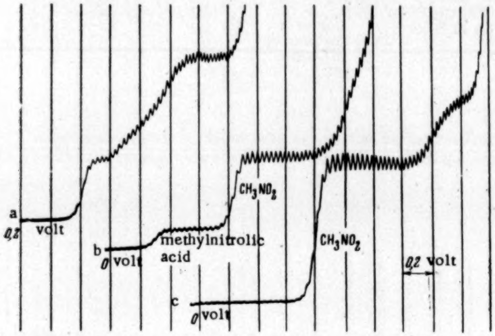

Fig. 5. Polarogram of methylnitrolic acid in alkaline a), and neutral solutions b), obtained by acidification of a mixture of CH_3NO_2 and $NaNO_2$.
a) 2 ml of 0.567 M CH_3NO_2 + 20 ml of 0.02 M $NaNO_2$. pH 7 $\xrightarrow{2\text{ M HNO}_3}$, pH 2.1, $\xrightarrow{1.2\text{ M NaOH}}$ pH 12.1, s = 1 : 100, 20°; b) 2 ml of solution a) + 7 ml of 0.2 M NaH_2PO_4; s = 1:200; pH 7.1; final concentrations of CH_3NO_2 calculated from the amount taken in experiment a) = 0.0041 mole/liter; in experiment b) 0.0091 mole/liter; c) polarogram of the control solution of nitromethane in a mixture of 0.2 M NaOH + 0.2 M NaH_2PO_4; [CH_3NO_2] is equal to 0.0014 M; s= 1:200; 20°;pH 7. X — methylnitrolic acid

Formation of nitrolic acids can be avoided by directly dissolving the mixture of the products obtained during the nitration of alkanes in a neutral phosphate buffer. This is evident from a consideration of the polarograms shown in Fig. 6 and which were obtained as follows; Three nitrations of propane were carried out under similar conditions (mixture of $4C_3H_8 + NO_2$; T = 250°; P_{initial} = 312 mm Hg; time for completion of reaction 22 minutes, corresponding to complete usage of the nitrogen dioxide). The products of the first nitration (Fig. 6.b) were dissolved in a buffer solution (0.2 M NaH_2PO_4 + 0.2 M NaOH; pH 7); while to the products of the second and third nitration was added 2 millimole of nitrogen dioxide. The products of the second nitration, with the added nitrogen dioxide, was dissolved first in 0.2 M LiOH, and then part of the alkaline solution was mixed with 0.2 M NaH_2PO_4 solution (Fig. 6 a). The products of the third nitration together with the added nitrogen dioxide were dissolved in a phosphate buffer (Fig. 6 c). In addition, for purposes of comparison, polarograms were taken of known methylnitrolic acid dissolved in a phosphate buffer with a pH of 6. When this was done a reduction wave

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•Polarographic waves are not observed in separate alkaline solutions of nitromethane and nitrogen dioxide.

with $\pi_{1/2}$ = -0.25 - 0.3 volt (see Fig. 7) was found. It is clear from this, that of the three polarograms in Fig. 6, only in the case of 6 a is there a wave for nitrolic acid ($\pi_{1/2}$ = -0.3 volt), in the case of 6 c it is absent.* It is obvious that on dissolving the nitration products in a neutral phosphate buffer there is not even a short-time formation of free nitrous acid.

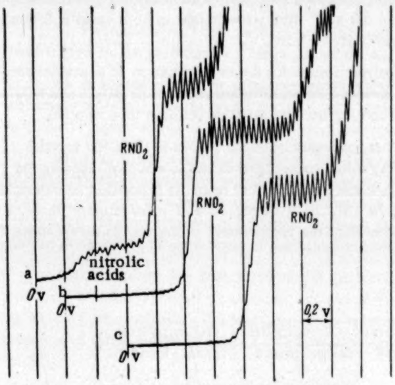

Fig. 6. Polarograms for solutions of mixtures of the reaction products with and with and without addition of NO_2; 20°; [RNO_2] determined on the basis of the wave with $\pi_{1/2}$ = 0.85 volt. a) To the reaction products was added 2 millimole of NO_2 followed by 20 ml of 0.2 M LiOH. Part of this solution was mixed with 0.2 M NaH_2PO_4 in the proportion of 2 : 4; s = 1: 200; pH 6.2 0.068 millimole of RNO_2 found. b) The reaction products were dissolved in 50 ml of a mixture of 0.2 M LiOH + 0.2 M NaH_2PO_4; s = 1: 500; pH 6.4; 0.135 millimole of RNO_2 found.

b) Determination of Alkylnitrities and Alkylnitrates in the Presence of NO_2. As indicated already, it is difficult to avoid formation of nitrolic acids on dissolving the nitration products in alkaline solution when they contain nitroparaffins and NO_2 (or HNO_2). This makes it very difficult to carry out a polarographic determination of alkylnitrites and alkylnitrates, since the reduction wave of the latter coincides with the reduction wave of nitrolic acid ($\pi_{1/2}$ = -0.65 volt in alkaline media). In order to determine total RONO and $RONO_2$ in the presence of nitrolic acids we made use of the fact that nitrolic acid remains in aqueous solution even when nitrogen is blown through the solution for a long time, while both RONO and $RONO_2$ are completely expelled by the nitrogen stream in 10-20 minutes at room temperature. For example, on blowing nitrogen through a) a 0.0017 M solution of C_2H_5ONO in 0.2 M LiOH (solution A), through b) an alkaline solution of methylnitrolic acid prepared by successively pouring together 2 ml of 0.056 M CH_3NO_2, 20 ml of 0.02 M $NaNO_2$, 0.45 ml of 2 M HNO_3, and 1.6 ml of 1.2 M NaOH (solution B), and c) through a mixture of 2 ml of solution A and 7 ml of solution B, it was found that ethylnitrite was removed from solution A and from mixture of solutions A and B to the extent of 99% in the course of 10 minutes, while the concentration of methylnitrolic acid in solution B, and in a mixture of solutions A and B, remained constant for not less than 35 minutes. Thus, in order to determine total alkylnitrates in the presence of nitrolic acids and the other nitration products in 0.2 N LiOH, first of all determine the total wave height of the nitrites, nitrates, and nitrolic acids with $\pi_{1/2}$ = -0.6-0.65 volt at 0°, and then blow nitrogen through the solution at room temperature until the height of the polarographic wave indicated is constant, and finally repeat the determination at 0°. The value obtained at 0° determines the amount of nitrolic acids. The difference between the first and third determinations at 0° corresponds to the sum of the alkylnitrites and alkylnitrates.**

c) Mixtures of Aldehydes and NO_2. Since, in the presence of NO_3^- (or NO_2^-), the origin for the reduction of Li^+ is shifted toward more positive potentials, the shift being greater ther higher the concentration of these ions, then, starting at some definite NO_3^- (or NO_2^-) concentration polarographic analysis of aldehydes becomes impossible. For example, when polarograms are taken of 0.0008- 0.0018 M solutions of formaldehyde in 0.2 M LiOH, determination of formaldehyde is impossible when the concentration of NO_3^- is greater than 0.01-0.05 mole/liter. For acetaldehyde this limit is lowered 10 times (0.001-0.005 mole/liter).

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*In the case of 6 b, nitrolic acid cannot be formed, since nitrogen dioxide is not present in the mixture of products.

**We used this method for determining nitrites (nitrates were absent) in the presence of nitrolic acids in the products obtained by the interaction of alkyl radicals and NO_2.

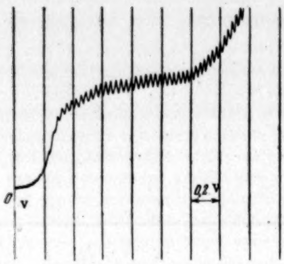

Fig. 7. Polarogram for methylnitrolic acid dissolved in a mixture of 0.2 M LiOH + 0.2 M NaH_2PO_4; s= 1:500; 20°; pH 5.6.

One way out in the case of the polarographic determination of formaldehyde would appear to be dilution of the alkaline solution so as to lower the NO_3^- (or NO_2^-) concentration. The success of such an approach is determined by the concentration of the aldehyde and of the NO_3^- (or NO_2^-) and their proportions. For the polarograph which we used, the limit is $1.5 \cdot 10^{-5}$ M formaldehyde when the determination is carried out at 25°, and $2 \cdot 10^{-4}$ M when the determination is carried out at 0° (the wave height in both cases is 2 mm for a sensitivity of 1:10).

Positive results for the determination of acetaldehyde can be obtained by preliminary removal of NO_2^- and NO_3^-, by supercooling the test alkaline solution in a vacuum.

Thus, on supercooling a 0.0002 M CH_3CHO solution, containing 0.015 mole/liter of NO_3^-, and then heating the trap with warm water for 1-2 hours, it is possible to determine 93% of the CH_3CHO (the presence of nitromethane leads to low results when the temperature of the trap is taken above 0°).

TABLE 8

Analysis of Synthetic Mixtures in the Presence of NO_2

Composition of the mixture	HCHO, m/liter		CH_3NO_2, m/liter		CH_3CHO, m/liter	
	taken	found	taken	found	taken	found
1ml 0,030 *M* HCHO; 4 ml 0,019 *M* CH_3NO_2; 0,5 ml 0,0136 *M* CH_3CHO; 14,5 ml 0,28 *M* LiOH; 0,2 m/mm NO_2, pH 12,2	0,0015	0,0013	Not determined		Not determined	
8ml 0,030 *M* HCHO; 4 ml 0,019 *M* CH_3NO_2; 4 ml 0,0136 *M* CH_3CHO; 2 m/mm NO_2; 4 ml 1 *N* $NaOH+NaH_2PO_4$, pH 5,75	not determined		0,0038	0,0037	not determined	
0,5ml 0.030 *M* HCHO; 5 ml 0,019 *M* CH_3NO_2 0,5 мл 0,0136 *M* CH_3CHO; 2 m/mm NO_2; 4 ml 1 *N* LiOH; 10 ml H_2O, pH 12,4*	not determined		not determined		0,00034	0,00033

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*See footnote on page 201.

d). Mixtures of Aldehydes, Nitromethane, and NO_2. Satisfactory results for the determination of acetaldehyde in the presence of nitromethane, formaldehyde, and NO_2 were obtained by the following technique. 5 ml of an aqueous solution of the aldehydes and of nitromethane, 0.2 M with respect to LiOH and prepared at 0°, was poured into a trap containing frozen nitrogen dioxide, and the whole mixed. The solution was supercooled at 0° by agitating it in the trap, cooled with liquid nitrogen, by means of a stream of nitrogen. Supercooling took about 5 hours. To the solution obtained was added at 0°, 0.5 ml of 0.1 M LiOH. Polarograms were also taken at 0°. It should be pointed out that on supercooling the alkaline solutions, a large part of the formaldehyde and nitromethane is lost (up to 90%). It is possible that nitromethane is precipitated as the salt of a nitrolic acid, which is not supercooled, while the formaldehyde forms hydrates with a low vapor pressure and is then polymerized on concentrating the solution.

The following results can be adduced as examples. In a mixture consisting of 0.125 ml of 0.0136 M CH_3CHO, 1.25 ml of 0.019 M CH_3NO_2, 0.125 ml of 0.030 M HCHO, 0.5 millimole of NO_2, 2.5 ml of H_2O, and 1 ml of 1 M NaOH (in such a mixture $[CH_3CHO] = 0.00034$ M) 0.00033 mole/liter of CH_3CHO was found.

General Method for the Analysis of Liquid Products in the Presence of NO_2

The analytical procedure adopted in the presence of nitrogen dioxide differs from the analytical method used in its absence in the following respects:

a) Nitroparaffins. For determination of the nitroparaffins, the nitration products should be dissolved in a buffer mixture of 0.2 M NaOH + 0.2 M NaH_2PO_4, containing an excess of NaOH such that, after diluting and neutralizing the NO_2, the pH of the solution should be 6-7. One cannot use a solution by mixing it with NaH_2PO_4, since on dissolving the LiOH, some of the nitroparaffins are converted into nitrolic acids.

b) Formaldehyde. The method remains unchanged, but as indicated already, formaldehyde cannot be determined in the presence of a large excess of NO_2.

c) Acetaldehyde. The nitration products are dissolved in 0.2 M LiOH at 0°, as indicated above. It is necessary to take LiOH in twofold excess with respect to the amount of NO_2 it is desired to neutralize. The method of supercooling at 0° in a stream of nitrogen, by the technique indicated above, is then used.

d) Alkylnitrates and Alkylnitrites are determined as described above. It must be emphasized that satisfactory results can only be obtained by taking polarograms in LiOH solution when all the manipulations are made rapidly and at a temperature not higher than 0°. It is recommended that the electrolytes be purged of oxygen by blowing nitrogen or hydrogen through them, before dissolving the reaction products in them, otherwise, during the purging process some of the reaction products will be lost.

This technique has been tried out on synthetic mixtures prepared by dissolving NO_2, frozen in a trap, in mixtures of solutions of nitromethane, acetaldehyde, and formaldehyde. One of the components was determined in each of the mixtures. The stability of the mixtures in the presence of NO_2^- and NO_3 was the same as in the absence of these anions (Table 5). The accuracy of the results obtained (Table 8) is not less than in the absence of NO_2.

As indicated above, the analytical method developed was used for the quantitative determination of the liquid products obtained by the thermal nitration of propane and methane, and by the low-temperature interaction of alkyl radicals with nitrogen dioxide. We were unable to detect any other waves on the polarograms apart from those belonging to the nitroparaffins, alkylnitrites, aldehydes, and nitrolic acids. It was also established that, on using the method developed, nitrogen oxides present in the nitration products do not give polarographic waves. The presence of the oxides only leads to the formation of nitrolic acids, and to a shift in the reduction potential of the base electrolyte.

The deviation between the results of parallel experiments did not, as a rule, exceed 10% of the values determined.

SUMMARY

A method has been developed for the quantitative polarographic analysis of mixtures of the liquid products obtained during the thermal nitration of alkanes, and during the low-temperature interaction of alkyl radicals and nitrogen dioxide; this method permits determination of total nitroparaffins, total alkylnitrites, formaldehyde, and total higher aldehydes, both in the absence and the presence of nitrogen dioxide.

Determination of formaldehyde in 0.2 M LiOH is possible as long as the NO_3^- concentration is not higher than 0.01-0.05 mole/liter.

When alkylnitrites and alkylnitrates are present together, the method gives their sum.

Polarograms of methylnitrolic acid have been obtained for the first time. In 0.2 M LiOH solution the polarogram for methylnitrolic acid consists of two waves, with $\pi_{1/2} = -0.6$ volt and $\pi_{1/2} = -1.0$ volt with respect to the saturated calomel electrode. Only one wave with $\pi_{1/2} = -0.6$ volt and $\pi_{1/2} = -0.6$ volt and $\pi_{1/2} = -0.25$--0.3 volt is observed in a buffer solution of 0.2 M NaOH + 0.2 M NaH_2PO_4 with a pH of 5-7.

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DETERMINATION OF GOLD BY AN ELECTROMETRIC NONCOMPENSATING METHOD

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The electrometric noncompensating method for the quantitative determination of gold is based on the reduction of Au^{III} or Au^{I} by ferrous sulfate to metallic gold in acid media at room temperature. The indicator electrode used is a gold wire, or a gold-plated platinum wire, while a sulfate-copper electrode is used as the auxiliary electrode; its construction is described in a previous article [1].

Electrodes which are short-circuited through a small external ohmic resistance R are used in electrometric noncompensating titration. An indicator – a needle galvanometer or microameter is connected in series in the circuit. It was established experimentally that the value of the potential differences of the short-circuited electrodes, (gold)ϵ_k and (the auxiliary)ϵ_a, and the strength of the polarization current I depends on the value of the external resistance R and the internal resistance r in accordance with Ohm's law

$$I = (\epsilon_k - \epsilon_a) / (R + r) \tag{1}$$

On short circuiting the electrodes through the external resistance R > 1000 ohms, the value of r remains so small that it can be disregarded in equation (1). Accordingly, the relation indicated above can be expressed by the equation

$$I = (\epsilon_k - \epsilon_a)/R \tag{2}$$

The potential of the gold electrode in the solution being titrated is determined by the concentration of Au^{III} and the value of R. In the noncompensating method for titrating Au^{III}, electrodes which are short circuited through a resistance of about 20,000 ohms are used. The potential of the sulfate-copper electrode does not depend on the composition of the solution being titrated, it is determined only by the composition of the electrolyte in the agar gel and the value of R. Under equilibrium conditions the sulfate-copper electrode has a potential of about 0.30 volt with respect to the normal hydrogen electrode. In solutions of Au^{III} and Au^{I} a gold electrode has a potential which is always more positive than the sulfate-copper electrode, accordingly in a close electrode pair, the first operates as a cathode and the second as an anode.

Under these conditions the following reaction occurs on the cathode

$$Au^{III} + 3e \rightarrow Au^{\circ}.$$

Another reaction, equivalent to the above, occurs on the copper electrode under the same conditions

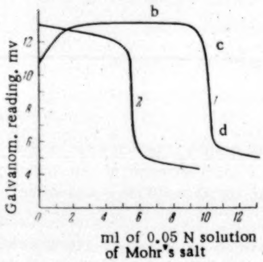
$$Cu^{0} \rightarrow Cu^{III} + 2e$$

The method described below for the determination of gold was developed for the analysis of jeweller's alloys, containing silver and copper, in addition to gold.

Experimental investigations were carried out with the aim of establishing the possibility of carrying out a direct titration of gold with a solution of Mohr's salt, without removal of nitrous acid and separation of AgCl

Synthetic solutions were prepared from $HAuCl_4$, $CuSO_4$, $AgNO_3$, and concentrated acids. The method developed has been checked in the Sverdlovsk Inspectorate of the Assay Service of the USSR Ministry of Finance.

A sample of test alloys was dissolved in a mixture of hydrochloric and nitric acids (aqua regia). During this process the gold and copper dissolve, while silver is precipitated as AgCl. The solution also contains excess hydrochloric and nitric acids.



1) Titration curve of $HAuCl_4$ with a solution of Mohr's salt; 2) titration curve for the part of the gold remaining after precipitation of the greater part of it with Mohr's salt.

The indicator apparatus used was a needle galvanometer with a 17 millivolt scale and R_r = 260 ohms. One galvanometer division corresponded to 0.2 millivolt or 0.78 μa. The test solutions were titrated with about a 0.05 N solution of Mohr's salt in 5% H_2SO_4 The electrode pair were closed through a resistance of 20,000 ohms. The solution was agitated by rotating the beaker placed on rotating table [2] rotating at 180 revolutions/minute.

Titration Curves. During titration of gold solutions, the galvanometer does not directly measure the difference in potentials $\Delta\epsilon$ of the closed electrodes, but the polarization current I. The latter is related functionally to $\Delta\epsilon$ in accordance with Ohm's law. In our case, only the gold electrode reacts to changes in the composition of the solution, accordingly, at constant R, the value of I will be proportionally related only to the potential of the gold electrode.

The curves obtained during the noncompensating method can reflect, depending on the coordinates chosen, the change in the current, of the potential differences of the closed electrodes. The curve shown in the diagram expresses the change in the potential of the gold electode during the titration of a solution of $HAuCl_4$

During titration of $HAuCl_4$ solutions, deposition of gold metal in the precipitate was not observed once. Over the part ab of the titration curve, the solution remained clear. Deposition of gold only occurred on the part bc and finished over the part cd. During this process, for the titration from a to b, i.e. to the beginning of the deposition of gold, 2/3 of the total amount of Mohr's salt taken altogether was used. On this basis it can be assumed that the reduction of Au^{III} to Au^0 proceeds successively in two stages:

$$Au^{III} + 2e \rightarrow Au^{I}$$
$$Au^{I} + e \rightarrow Au^{\circ}.$$

During the first stage, AuCl which is soluble in water is formed, consequently the solution remains clear.

The standard (normal) electrode potential of gold in a solution of its ions has not yet been determined accurately. According to Latimer [3] it is given by

$$\varphi^{\circ}_{Au^{I}/Au^{\circ}} = \sim 1{,}68 \quad \text{and} \quad \varphi^{\circ}_{Au^{III}/Au^{\circ}} = 1{,}50,$$

while according to Lur'e [4] it is given by

$$\varphi^{\circ}_{Au^{I}/Au^{\circ}} = 1{,}50 \quad \text{and} \quad \varphi^{\circ}_{Au^{III}/Au^{\circ}} = 1{,}29 \quad \text{volts on the hydrogen scale}$$

The shape of the titration curves for solutions of $HAuCl_4$ completely agrees with the ratio of the values of the electrode potentials of the gold electrode indicated above. The rise on the titration curve corresponds with an increase in the potential of the gold electrode which arises as a consequence of the appearance in the solution of Au^{I} ions in increasing concentrations. The absence of a maximum at the point $\underline{b}$ can be explained by the small dissociation of $[AuCl_4]^-$ and AuCl (or $AuCln^{1-n}$). For the first, $K = 5 \cdot 10^{-22}$, but for the second, K is unknown.

As indicated above, during the titration of the test solutions there occurs a partial loss of the gold, as a result of its deposition on the gold cathode. The amount of this loss in grams can be found by means of the equation

$$m = IMt/zF.$$

In this equation $\underline{I}$ is the current strength in amp./second; $\underline{M}$ is the atomic weight of gold; $\underline{t}$ is the duration of an experiment in seconds; $\underline{z}$ is the charge on the gold cation; and $\underline{F}$ is the Faraday constant. By comparing equations (2) and (3) we get

$$m = \frac{(\varepsilon_k - \varepsilon_a)Mt}{RzF}.$$

From the last two equations it is clear that the extent of the loss of gold on the gold electrode will be proportional to the current of the working electrode pair, the duration of the experiment and the value of the potential of the gold electrode, and will be inversely proportional to the value of the external resistance.

In our experiments the value of $\underline{I}$ did not exceed 40 μa, while the titration lasted not more than 5 minutes. Under such conditions the amount of gold lost on the cathode during the reduction of Au^{III} to the metal amounts to

$$m = \frac{40 \cdot 10^{-6} \cdot 197 \cdot 5 \cdot 60}{3 \cdot 96500} = 8{,}5 \cdot 10^{-6} \text{ g}$$

while during the reduction of Au^{I} the amount of gold lost should be three times greater.

For many technical methods of analysis such a loss would not be particularly important, but for the analysis of gold alloys which demands especially high accuracy, the extent of this loss cannot be ignored.

During the electrometric noncompensating method of analysis the loss of gold on the cathode can be cut down as follows:

1. By increasing the external resistance R by using a more sensitive galvanometer. The use of mirror galvanometers make it possible to cut down the amount of gold lost 10-20 times;

2. By cutting down the time taken for titrating, and also by the immediate addition of a large portion of the Mohr's salt solution to the solution being titrated, with subsequent titration to the end with the same solution of Mohr's salt of the remaining small amount of gold. This technique has been used in the procedure given below for the determination of gold in jeweller's alloys.

3. The experimental error can also be reduced to a minimum by keeping the titration time a constant. Thus, by using an empirical titer, or by introducing a correction for the gold precipitated, analysis of gold alloys can be carried out with an accuracy of 0.5-to 1.0 or 0.05-0.1%.

Titration Conditions. The following facts were established in the course of some special experimental studies.

During titration of gold, Fe^{2+} cations are not oxidized by nitric acid in the presence of HCl, accordingly there is no need to remove the nitric acid from the solution after dissolving the gold.

AgCl precipitates do not interfere with titration of gold.

Copper salts not only do not interfere, but even exert a favorable effect on the shape of the titration curves; accordingly copper in the form of $CuSO_4$ is deliberately added to the solution being titrated.

Hydrochloric acid has an unfavorable effect both on the shape of the titration curves and on the amount of

Mohr's salt used up in the titration; the jump on the titration curve decreases with increasing hydrochloric acid concentration, while the amount of Mohr's salt used up increases.

Good results are obtained in the presence of orthophosphoric acid. The curves show exceptional reproducibility and have a shape which is suitable for establishing the endpoint. Chlorides, nitrates, sulfates, Cu^{2+}, and AgCl do not interfere with titration of gold in the presence of H_3PO_4

The results of our studies made it possible to devise the following fairly simple analytical scheme; an aliquot of alloys is dissolved in concentrated aqua regia, this solution is neutralized with concentrated alkali solution, after which the solution is re-acidified with phosphoric acid, and is finally titrated with Mohr's salt.

Determination of the Expenditure of Mohr's Salt. It was pointed out above that in order to cut down the amount of gold lost on the cathode, it is expedient to add a large amount of the Mohr's salt to the solution being titrated right at the beginning, the amount added being such that some gold is left in the solution ;the gold remaining is then titrated to the end with the same solution of Mohr's salt. The Mohr's salt was standardized against pure gold.

EXPERIMENTAL PROCEDURE

An aliquot of rolled, finely cut gold alloys, of quality 583,(about 0.18 g) is weighed on an assay balance to the fifth decimal place. It is transferred to a dry 250-300 ml chemical beaker and covered with 15 ml of a mixture of $HCl + HNO_3$ (3:1), the beaker is covered with a watch glass and heated on a sand bath or on an open electric hotplate.

The mixture of hydrochloric and nitric acids should be prepared fresh daily from the pure concentrated acids. In such a mixture the alloy dissolves very readily without deposition of AgCl. When the acids used are not concentrated enough (sp. gr. less than 1.19 and 1.40) AgCl is deposited on the lumps of alloy and strongly hinders dissolution of the alloy.

When the alloy is being dissolved, the solution should not be shaken, otherwise solution which gets on to the walls will sputter and may overheat. Neither should the solution be evaporated to dryness. In the latter instance and in the case of overheating on the beaker walls, partial decomposition of auric to aurous chloride may occur ($AuCl_3 \rightarrow AuCl + Cl_2$).

After the alloy has dissolved and the solution has been cooled, the watch glass and the beaker walls are washed with distilled water. During this process AgCl is deposited. Washing should be carried out with the minimum amount of water.

To the acid solution is added 5.0 ml of 10% $CusO_4$ solution prepared from chemically pure $CuSO_4 \cdot 5H_2O$ free from $FeSO_4$. The solution is neutralized with 30% NaOH (or KOH) until a black precipitate forms (Ag_2O).

In order to dissolve the precipitate formed, and in order to create an acid medium, 5.0 ml of 80% H_3PO_4 free from phosphorous acid H_3PO_3 is added to the solution. The AgCl precipitate remaining does not interfere with titration of gold.

To the phosphoric acid solution is added by means of a pipet exactly 25.00 ml of approximately 0.05 N Mohr's salt solution in 5% H_2SO_4. During this stage the bulk of the gold is precipitated, the remaining gold is then titrated with the same solution of Mohr's salt to the end point. The amount of Mohr's salt used is determined from the titration curve as indicated above.

After completing the titration, the precipitate of gold and AgCl is filtered off, washed with water, and then with concentrated ammonia in order to remove the AgCl. The filter plus gold are dried and calcined in a porcelain crucible until the powdered gold sinters.

Standardization of Mohr's Salt. The Mohr's salt can be standardized either against pure gold of not less than 999.9 quality, or by means of a sample of alloy whose gold content is accurately known. During the standardization of Mohr's salt by means of pure gold or by means of a gold alloy, all the operations described above for preparing test material for analysis, as well as the titration itself are carried out exactly the same way as outlined in the above procedure. About 0.110 g of pure gold, weighed out to the fifth place, is taken.

SUMMARY

An electrometric noncompensating method has been developed for the determination of gold in jeweller's alloys by titration with a solution of Mohr's salt.

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SEPARATION OF THORIUM FROM THE RARE-EARTHS BY MEANS OF TANNIN*

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Schoeller [1] who successfully used tannin for separating tantalum and niobium, indicated that thorium is quantitatively precipitated in a neutral tartrate solution together with aluminum, iron, chromium, titanium, zirconium, vanadium, niobium, tantalum, and uranium. The rare-earths are quantitatively precipitated by tannin in the presence of excess ammonia, both in solutions containing tartaric acid and also in the absence of the latter. Information regarding the possibility of separating thorium and the rare-earths by means of tannin, is, however, nonexistent.

TABLE 1

pH Values at which Hydroxides Start of Precipitate

Cations	Anions		
	Cl^-	NO_3^-	SO_4^{2-}
Ce^{IV}		3,1[4]	
Th^{IV}	3,51[4]	3,57[4]	3,53[4]
Sc^{III}	4,90[5]		4,80–4,90[5]
Lu^{III}		6,30[6]	6,18[6]
Yb^{III}		6,30[6]	6,18[6]; 6,16[7]
Tu^{III}		6,40[6]	6,21[6]
Er^{III}		6,76[6]	6,50[6]
Gd^{III}		6,83[6]	6,75[6]
Eu^{III}		6,82[6]	6,68[6]
Sm^{III}	6,83[4]	6,92[6]; 6,83[4]	6,70[6]
Y^{III}	6,78[4]	6,95[6]; 7,39[6]	6,83[6]; 7,39[6]
Nd^{III}	7,02[4]; 7,40[7]	7,31[6], 7,02[4]	6,95[6]; 6,73[7]
Pr^{III}	7,06[4]	7,35[6]	7,17[6]; 6,98[7]
Ce^{III}	7,41[4]	7,60[6]; 8,10[6]	7,35[6]; 7,07[7]
La^{III}	8,03[7]	7,82[6], 8,35[4] 8,71[6]	7,41[6]; 7,61[7]

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*This work was carried out in 1949.

Neish [2] a long time before the appearance of Schoeller's paper noted that "tannin quantitatively precipitated thorium, but does not precipitate cerium, lanthanum, and didymium." Venkataramanian, Satyanarayanamurthy, and Rao [3], in addition to other methods of separating thorium from the cerium subgroup of the rare-earths, very briefly described a method based on the precipitation of thorium by means of tannin from acetic acid solution.

The present article contains a description of another method of solving the problem of separating thorium from the cerium, as well as from the yttrium subgroup of the rare-earths, by means of tannin.

The use of tannin in analytical chemistry is based on its colloidal-chemical properties [1]. Tannin is a mixture of the esters of digallic acid and glucose, the most important of which is pentadigalloglucose—a material with a molecular weight of about 1700. Aqueous solutions of tannin, like those of many other high molecular weight polyelectrolytes, contain fairly large negatively charged particles, and possess some properties which are typical of colloidal solutions. With highly dispersed positively charged hydrosols of the hydroxides or basic salts of certain metals, tannin, under certain conditions (temperature, concentration, pH, etc.) forms adsorbed compounds which separate out of solution in the form of large flocs.

The hydroxides of the trivalent rare-earths, as a rule, are quantitatively precipitated in alkaline media.

Some of them, as is evident from Table 1, start to precipitate at a pH of 6.2. Thorium hydroxide starts to precipitate in a more acid medium at pH 3.5. The pH values indicated are almost independent of the nature of the anions present, and remain constant for dilute nitric, sulfuric, and hydrochloric acid solutions [4]. The existence of a fairly considerable difference between the pH values at which the rare-earths and thorium are precipitated, serves as a basis for their quantitative separation.

For preparing the working solutions of thorium, a preparation of thorium nitrate $Th(NO_3)_4 \cdot 4H_2O$ was used, in which the amount of rare-earths, present as impurities, did not exceed 0.1% as established by x-ray spectrochemical analysis. The starting material used for preparing solutions of the rare-earths in nitric acid, was a mixture of the oxides having the following composition according to the results of x-ray spectrographic analysis carried out by I. B. Borovskii:

CeO_2	48%	Y_2O_3	4 %
La_2O_3	23	Gd_2O_3	1,2
Pr_6O_{11}	4	Tb_4O_7	0,3
Nd_2O_3	16	Dy_2O_3	0,3
Sm_2O_3	3	PbO	0,1

The working solutions of thorium nitrate, and of the mixture of the nitrates of the rare-earths, were standardized gravimetrically by weighing the oxides obtained by calcining the hydroxides, oxalates, and dry residues obtained on evaporating their solutions to dryness.

As tests showed, tannin quantitatively precipitates thorium in approximately 0.005 N nitric or hydrochloric acid solution (Table 2 and 3).

TABLE 2

Determination of Thorium in Nitric Acid Solutions
(0.0100 g ThO_2 taken)

HNO_3, N	ThO_2 found, g	Error, g
0,004	0,0099	—0,0001
0,006	0,0097	—0,0003
0,006	0,0100	—0,0000
0,009	0,0090	—0,0010
0,009	0,0091	—0,0009
0,011	0,0091	—0,0009
0,011	0,0085	—0,0015

For complete precipitation of thorium the amount of tannin taken should be five times the weight of thorium as the dioxide, and not less than 1 g per 100 ml of solution. The presence of ammonium chloride or nitrate in small amounts up to 1 g per 100 ml of solution makes it possible to get more dense precipitates which are easier to filter. Concentrations of ammonium salts in excess of 2 g per 100 ml, however, should be avoided, otherwise the thorium will not be precipitated completely.

Sulfate ions should be completely absent; even small amounts of sulfate lower the completeness of thorium precipitation considerably. Thus, instead of 0.0964 g of ThO_2, the amount found during precipitation with tannin in the presence of about 0.07 g SO_4^{2-} was found to be only 0.0565 g ThO_2.

Such considerable incomplete precipitation is most probably explained by the formation of the readily soluble complex salt $Th(SO_4)_2(NH_4)_4$ [8].

The tannin method of determining thorium (Table 3) posesses a rather rare sensitivity for analytical determinations of $0.0004 : 1000 = 4 \cdot 10^{-7}$.

Separation of Thorium from the Rare-Earths

Preliminary experiments showed that under those conditions where thorium is precipitated quantitatively, the rare-earths are not precipitated by tannin. The rare-earths are not precipitated in 0.005 N hydrochloric acid or nitric acid by tannin, only when dilute solutions are used, and their content in 100 ml does not exceed about 0.5 g. On increasing their concentration to 2 g per 100 ml, the rare-earths are precipitated in considerable amounts. In one such experiment the weight of their oxide precipitates amounted to 1.3% or 0.0265 g.

TABLE 3

Determination of Thorium in 0.005 N Hydrochloric Acid Solutions

ThO_2 taken, g	Volume of solution, ml	ThO_2 found, g	Error, g	ThO_2 taken, g	Volume of solution, ml	ThO_2 found, g	Error, g
0.0097	100	0.0096	−0.0001	0.0019	1000	0.0019	0.0000
0.0097	100	0.0098	+0.0001	0.0004	1000	0.0003	−0.0001
0.0019	1000	0.0016	−0.0003	0.0004	1000	0.0003	−0.0001

Experiments on the separation of thorium from the rare-earths were carried out mainly by the technique described below, both in nitric and in hydrochloric acid solutions. In the latter instance, when it was necessary to reprecipitate, the tannin-thorium precipitate was dissolved in hot hydrochloric acid (1:3) and reprecipitation carried out under the same conditions as those used for the first precipitation. One drawback of this method is that there occurs partial decolorization of the indicator (methyl red) during neutralization, which complicates establishment of the requisite acidity of the solution. Reprecipitation of the thorium precipitate by the same method, but using nitric acid solutions, proved impossible because of the oxidation of the tannin. The solution acquired such an intense brown color that it was impossible to establish the color change of the indicator. The precipitate obtained was, accordingly, calcined to thorium dioxide, and the latter, after weighing, was brought into solution by fusing it with potassium pyrosulfate.

TABLE 4

Separation of Thorium and the Rare-Earths by Means of Tannin

Taken, g		Volume of solution, ml	Found, g			Error	
			ThO_2				
ThO_2	TR_2O_3		First precipitation	Second precipitation	TR_2O_3	ThO_2	TR_2O_3
0,4162	0,0049	400	0,4164	—	0,0052	+0,0002	+0,0003
0,3232	0,0050	•	0,3235	—	—	+0,0003	—
0,3242	0,0050	•	0,3248	—	—	+0,0006	—
0,2705	0,2171	•	0,3062	0,2707	0,2172	+0,0002	+0,0001
0,0995	0,0990	300	0,1001	—	—	+0,0006	—
0,0471	0,1243	200	0,0486	0,0468	0,1243	−0,0003	0,0000
0,0471	0,1243	•	0,0485	0,0470	0,1248	−0,0001	+0,0005
0,0236	0,0248	•	0,0238	0,0233	0,0245	−0,0003	+0,0003
0,0050	2,0	500	0,0047	—	—	−0,0003	—
0,0024	2,0	600	0,0266	0,0025	—	+0,0001	—
0,0024	2,2	•	0,0920	0,0026	—	+0,0002	—

The results given in Table 4 show that separation of thorium and the rare-earths * proceeds satisfactorily in intric acid solutions, even when the thorium is only precipitated once, as long as the ratio of $ThO_2:Tr_2O_3$ is greater than unity and when separation is carried out in relatively dilute solutions. In practice, however, it is necessary to resort to reprecipitation. In all cases where satisfactory separation was achieved, the thorium dioxide was white in color, sometimes with a weak rose tint.

Method Used for Separating Thorium from the Rare-Earths.

Precipitation of Thorium. To a cold solution of the nitrates of thorium and the rare-earths free from quadrivalent cerium, sulfate ions, and hydrogen peroxide, and equal in volume to approximately half the final volume**,and containing a small amount of free nitric acid and a few drops of methyl red, ammonia is added dropwise and with stirring, until the color of the solution changes into a pure yellow. Nitric acid (sp.gr. 1.38-1.40 dilute with water in the proportion of 1:4) is then added slowly,dropwise,and with careful agitation of the solution, until the color changes to red; 3 drops per 100 ml of the final volume is then added in excess (assuming that the volume of one drop is 0.05 ml). When the concentration of the elements which we are interested in is low,then on neutralization, the precipitate of hydroxides only appears when the indicator shows an alkaline reaction; on subsequent acidification of the solution, the precipitate disappears. When appreciable amounts of these salts are present, a precipitate may appear before the solution shows an alkaline reaction, and will persist until the solution is acidified to 0.005 N; this will not interfere with the subsequent analytical procedure.

To the acidified solution is added: 0.5 g of ammonium nitrate and 1 g of tannin each(per 100 ml of the final volume) in the form of a filtered, aqueous solution; water is finally added to bring the volume up to the necessary value. When there is an appreciable amount of thorium, after addition of tannin, the white flocculent precipitate appears immediately in the cold; when the amount of thorium is low the precipitate only appears on heating. The solution contained in a beaker covered with a watch glass is heated to the boiling point. After boiling for a short time (1 minute) the hot solution is filtered through a filter paper of average density (white band). Before filtering, it is useful to add some macerated paper. When the first portion of filtrate is turbid it is recombined with the unfiltered material and passed through the filter again. The precipitate is washed with hot 0.25% tannin solution containing a small amount of ammonium nitrate (2-5 g in 1 liter). The well washed precipitate is calcined in a platinum crucible and weighed as ThO_2.

Precipitation of the Rare-Earths. Although tannin in an ammoniacal medium precipitates the rare-earths quantitatively, this method must be used with caution since the precipitate formed occupies a very large volume. When the amount of the rare-earths is small, a small excess of ammonia is added to the boiling filtrate and wash liquours from the tannin-thorium precipitate. After boiling for a short time the precipitate is transferred to a filter (red band) and washed with the same tannin solution as that used for washing the thorium precipitate. The washed precipitate is finally calcined and weighed.

It is better to precipitate larger amounts of the rare-earths with oxalic acid. But, since oxalic acid does not precipitate them completely quantitatively, the "traces" — sometimes amounting to some milligrams — remaining in the filtrate are precipitated completely with ammonia as described above. In this case, however, in addition to the "traces" of the rare-earths, other cations are also sometimes precipitated; these other ions (Ca, Fe, etc) get into the solution from insufficiently pure reagents, apparatus, etc. In order to free the precipitate from impurities, the "calcined "traces" of the rare-earths are dissolved in nitric acid and reprecipitation carried out with oxalic acid in the smallest possible amount of solution (20-30 ml).

Reprecipitation of Thorium. When the mixtures of thorium oxide and the rare-earths, prior to their separation, are colored more or less intensely brick-brown by elements of the cerium group, it is possible to get an estimate of the purity of the calcined thorium oxide from its color, since pure thorium dioxide is absolutely white in color. When the cerium subgroup is absent in the original mixture, it is not possible to estimate the degree of

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*On changing the weight ratio of ThO_2: TR_2O_3 from 1:900 to 80: 1.

**Separation of the elements is most efficient when their concentration in solution is low, but it is not always possible to use strongly diluted solutions. In practice, for the separation of thorium and the rare-earths it is possible to use the following final volumes as a function of the weight of their oxides:

Weight of the oxides (g)	up to 0.03	0.10	0.20	0.30	0.50 and higher
Volume of solution, ml	100	200	300	400	600

separation of thorium on the basis of the color of its dioxide, since the oxides of the yttrium group are also white or almost white, with yellow (Eu), rose (Er), and green (Tb) tints. When it is not possible to use x-ray spectrographic methods, some idea of the purity of the ThO_2 may be gained by an indirect method — by repeated precipitation of the thorium with tannin and comparing the weight of the dioxide with its weight after the first precipitation. Agreement between the results within the limits of experimental error indicates that the thorium dioxide is sufficiently pure.

For purifying it from rare-earths present as impurities, the thorium dioxide is fused with potassium pyrosulfate. After dissolving the melt in hot water acidified with nitric acid, thorium hydroxide is precipitated with ammonia. In order to achieve as complete a removal of sulfate ions as possible, the thorium hydroxide is dissolved in nitric acid and is again precipitated with ammonia. Such reprecipitation is repeated until the thorium is finally precipitated with tannin as described above. Usually, after precipitation with tannin, pure thorium dioxide is obtained. In the combined filtrates from all the thorium precipitates obtained during its purification, the rare-earths are precipitated in the form of the tannin complex and then reprecipitated with oxalic acid in the smallest possible volume.

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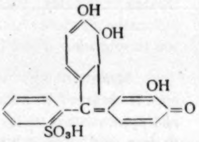
THE PHOTOMETRIC DETERMINATION OF ZIRCONIUM IN PHOSPHORITES BY MEANS OF PYROCATECHOL VIOLET

Yu. A. Chernikhov, V. F. Luk'yanov, and E. M. Knyazeva

Pyrocatechol violet (3,3',4'-trihydroxyfuchsone-2"-sulfonic acid) was suggested as an indicator for the complexometric titration of various elements in 1954 [1], and has found wide application for this purpose [2].



Flaschka and Sadek [3] were the first to use pyrocatechol violet for the qualitative detection of zirconium; subsequently, Flaschka and Farah [4] developed a method for the quantitative determination of small amounts of zirconium in solutions of its pure salts and in synthetic mixtures.

We have made a study of the interaction of zirconium with pyrocatechol violet and have chosen the optimum conditions for the photometric determination of zirconium both in solutions of its pure salts and in natural materials.*

Pyrocatechol violet was synthesized according to [5] but with some small changes.

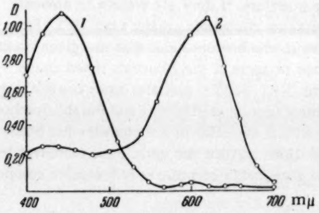


Fig. 1. Light absorption curves for solutions of the complex of zirconium with pyrocatechol violet, and for a solution of the reagent; pH 5.4.
1) $1 \cdot 10^{-5}$M pyrocatechol violet; 2) a solution of the complex 30 minutes after mixing $1 \cdot 10^{-4}$ M $ZrOCl_2$ with $1 \cdot 10^{-4}$ M pyrocatechol violet solution.

A comparison of the light absorption curves of solutions of the reagent, and of solutions of the complex formed between the reagent and zirconium (Fig. 1.) shows that it is possible to determine zirconium in the presence of excess reagent, since in the region where the maximum absorption of the zirconium complex occurs-at a wave length of 620 mμ - the reagent itself exhibits insignificant light absorption (the maximum absorption for the reagent occurs at 445 mμ).

Since pyrocatechol violet is also an acid-base indicator, a necessary condition for the determination of zirconium (as pointed out by the authors in [4]) is the maintenance of a constant pH by the use of an acetate buffer with a pH of 5.2-5.4. In this pH range the solution of the reagent has a yellow color, while the color for solutions of the complex with zirconium is blue.

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*Hafnium gives a similar reaction with pyrocatechol violet.

It should be pointed out that formation of the complex compound proceeds more rapidly after treating solutions of zirconyl chloride with concentrated acids (nitric, hydrochloric, and perchloric acids), as indicated below in the description of the determination of zirconium. This phenomenon was not discussed by Flaschka and Farah, but, as is evident from Table 1, such a preliminary treatment is of very considerable importance. The light absorption of solutions of the zirconium complex which have not been given a preliminary treatment with acids is considerably less than solutions treated with acids. Formation of the complex of zirconium with pyrocatechol violet is connected with the state of the zirconium ion in solution. There is published data on this question [6-9].

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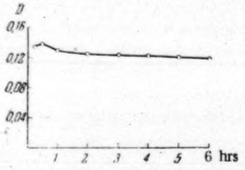

Fig. 2. Stability of the zirconium-pyrocatechol violet complex with time.

Maximum light absorption of solutions of the zirconium complex is observed 30 minutes after mixing the solutions of zirconium and pyrocatechol violet. After 1-2 hours the light absorption starts to drop, and after 18 hours amounts to 15-25% (Fig. 2).

Pyrocatechol violet is a highly sensitive reagent for the determination of zirconium. The color given by 0.1 γ of Zr in 1 ml of solution is quite distinct. The most suitable range for the photometric determination of zirconium covers from 5 to 70 γ of Zr in 50 ml; over this range the solutions conform to Beer's law (Fig. 3).

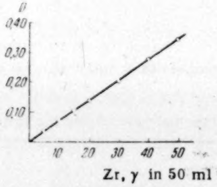

Fig. 3. Calibration curve for the determination of zirconium with pyrocatechol violet (FEK-M photocolorimeter, green filter, 20 mm cell).

When zirconium is determined in the presence of Complexon III at pH of 5.2-5.4, the alkali and alkaline-earth elements do not interfere, whatever their amounts. Other elements – Al, Fe^{3+}, Be, Ti, Th, UO_2^{2+}, Bi, V, Mo, W, Co – can be tolerated at ratios to zirconium of 100:1. Ions which possess an intrinsic intense color, such as Cu and Ni, may interfere, if they are present in amounts exceeding a ratio of metal to zirconium greater than 10:1. From what has been said above it can be concluded that the given method can be used for the analysis of alloys which contain zirconium and one or more of the elements listed above. Cl^-, NO_3^-, ClO_4^-, and SO_4^{2-} (in moderate amounts) can be present. F^-, PO_4^{3-} and also other complexing anions such as tartrate, oxalate, citrate, etc. interfere. A distinguishing feature of Flaschka and Farah's method [4] is that the reference solution used is a part of the test solution in which the color of the complex has been destroyed by addition of fluoride ions. Since fluoride ions in acid solutions corrode the cells, and, moreover, lead to complications when the test solution contains elements which also give stable complexes or insoluble compound with them (Fe, Al, Be, and Ca) we did not use their method.

In our variant the reference solution is a solution of pyrocatechol violet in an acetate buffer.

Determination of zirconium in solutions of its pure salts consists of the following.

An aliquot of a hydrochloric or nitric acid solution containing not more than 70 γ of Zr is placed in a 50 ml beaker; 5 ml of concentrated hydrochloric acid is added and the solution evaporated to a volume of about 0.5 ml. The solution is transferred to a 50 standard flask and the beaker rinsed out with three lots of 4-5 ml of water. 1 ml of 0.05 M Complexon III solution is added and the contents of the flask thoroughly mixed. The solution is neutralized with ammonia using methyl red as indicator (1 drop of 0.001% aqueous alkali solution), dilute hydrochloric acid is then added until the solution is weak-rose in color. 15-20 ml of acetate buffer is added (pH 5.2-5.4) followed by 4 ml of a 0.001 M (about 0.04%) solution of pyrocatechol violet; the solution is made up to the mark with buffer solution and the whole carefully mixed.

The optical density is measured 30 minutes afterwards, using a FEK-M photocolorimeter with a 20 mm cell, and a green filter. The reference solution is a mixture of 4 ml of 0.001 M (0.04%) pyrocatechol violet in the acetate buffer (pH 5.2-5.4), in a volume of 50 ml. The zirconium content is determined from a calibration curve which is constructed in the same way. For the preparation of a standard solution of zirconium see [10].

TABLE 1

Effect of Preliminary Treatment of $ZrOCl_2$ Solutions with Acids, on the Light Absorption of Solutions of the Complex of Zirconium and Pyrocatechol Violet

Zr taken, γ in 50 ml	Optical density of the solution	
	Without treatment of $ZrOCl_2$ with acids, HCl, HNO_3, $HClO_4$ *	After treatment of $ZrOCl_2$ with acids, HCl, HNO_3, $HClO_4$ *
5	0,032	0,039
10	0,054	0,071
15	0,070	0,097
20	0,082	0,134
30	0,094	0,198
40	0,140	0,262

*The mean values given for the optical density were obtained on treating the solutions of zirconyl chloride with each acid taken separately.

TABLE 2

Determination of Zirconium in Phosphorites

ZrO_2 found by the photometric method, %	Mean value	ZrO_2 found by the gravimetric phosphate method % *	ZrO_2 determined spectrographically, % **
0,73; 0,74; 0,76; 0,74	0,74	0,73	—
0,84; 0,82	0,83	0,81	0,89
1,13; 1,14: 1.15	1,14	1,09	1,26
0,12; 0,12	0,12	—	0,14
0,09; 0,09; 0,08	0,09	—	0,09
0,40; 0,40; 0,40; 0,41	0,40	—	0,36
0,69; 0,71	0,70	0,68	—
1,13; 1,13; 1,15	1,14	1,26	—

*The theoretical factor of 0.463 was used for converting the phosphate to ZrO_2.

**The analyses were carried out by M. A. Petrova

For determination of zirconium in sulfuric acid solutions, an aliquot of the solution is evaporated on a sand bath to dryness until white fumes of sulfuric acid cease to be evolved; the dry residue is treated with 5 ml; it is transferred to a standard 50 ml flask and the procedure described above then followed.

Zirconium is determined in phosphorites as follows: 0.2-0.5 g of test material, depending on the expected zirconium content, is heated with 40 ml of nitric acid (1:3) for 15-20 minutes on a sand bath the solution being contained in a 200-250 ml beaker covered with a watch glass. Since zirconium is found in phosphorites as the mineral zircon ($ZiSiO_4$), after treatment with acid, the zirconium remains in the form of an insoluble residue. The residue is quantitatively transferred onto a filter paper (blue band) and carefully washed with hot water. Filter plus residue are placed in a platinum basin, in which they are dried, ashed, and finally calcined in a muffle for 20-30 minutes. The basin is cooled and 1-3 g of potassium bifluoride is added, the mixture is fused in a muffle until a transparent melt is obtained.

To the cooled melt is added 15-20 ml of concentrated sulfuric acid and the whole evaporated on a sand bath until copious fumes of sulfuric acid are evolved. On cooling, the sulfuric acid solution is transferred from the basin into a 250 ml standard flask. in which it is made up to the mark with water and thoroughly mixed.

For determination of the zirconium, an aliquot of this solution, containing from 5 to 70 γ of Zr, is transferred to a beaker and free sulfuric acid removed by evaporation to dryness; 5 ml of concentrated hydrochloric acid is added to the dry residue and the procedure outlined above for solutions of pure zirconium salts then followed.

SUMMARY

A photometric method is described for determining from 5 to 70 γ of zirconium in 50 ml of solution by means of pyrocatechol violet. The solutions of the complex of zirconium with pyrocatechol violet conform to Beer's law. Methods have been developed for determination of zirconium in solutions of its pure salts and in phosphorites.

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DETERMINATION OF THE RATIO OF THORIUM TO URANIUM IN MINERALS AND ORES BY MEANS OF THICK-LAYER PHOTOGRAPHIC PLATES

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The thick-layer photographic plate method has been successfully used for studying the distribution of radioactive elements in rocks [1-8]. This method can be used for evaluating the amount of radioelements in materials [7,9]. For this purpose, the samples are used in their natural form (transparent sections, etc) without converting them into a powder or solution, as is usually done in the course of radiometric or radiochemical methods. Determination of the relative contents of uranium and thorium is possible on the basis of measurements of the path lengths of the α-particles in the emulsion. High energy particles are emitted by RaC', AcA, and ThC'. The α-particles emitted by RaC' from the uranium family, and by ThC' from the thorium family, are characterized by their initial energy, and, accordingly, by their path lengths in air, which at 15° and normal pressure are equal to 6.91 and 8.57 cm, respectively.

According to our measurements, the mean path length of α-particles in a photoemulsion of the type A-2 No. 2289 NIKFI is equal to 38.5 μ in the case of RaC' and 47.3 μ for ThC'. This difference of 9 μ in the path lengths of the α-particles makes it possible to calculate the number of α-particles from ThC' and RaC' fairly accurately, and, accordingly, it becomes possible to determine the relative contents of thorium and uranium in a sample.

Curie [9] in 1946 theoretically demonstrated the possibility of determining the relative contents of radioactive elements in thick layers of a mineral. According to Curie, the number of α-particles emitted from 1 cm^2 of the surface of a sample per second, with a path length greater than ρ, is equal to

$$n = \frac{N}{4} k (R - \rho), \tag{1}$$

where N is the number of α-particles emitted by 1 cm^3 of a material per second; R is the path length in air; ρ is the minimum residual path length which can be fixed, and k = R'/R (R' is the path length of the α-particles in the test material).

When a radioactive material contains thorium, uranium, and actinouranium at the same time, the longest traces will belong to the α-particles emitted by ThC (8.57 cm), RaC' (6.91 cm), and AcA (6.46 cm). Accordingly, the number of α-particles which have a path length greater than 7 cm in air, and, undoubtedly belong to ThC', will be given by

$$n_1 = 0{,}663 \frac{N_{\text{Th}}}{4} k (8{,}57-7); \tag{2}$$

where n_1 is the number of α-particles with a path length in air greater than 7 cm.

The total number of α-particles (n), having a path length in air greater than 5.8 cm is given by

$$n = 0{,}663 \frac{N_{\text{Th}}}{4} k (8{,}57-5{,}8) + \frac{N_{\text{V}}}{4} k (6{,}91-5{,}8) + \frac{N_{\text{V}}}{4} k\, 0{,}04 (6{,}46-5{,}8). \tag{3}$$

Particles which have a path length in air between 5.7 and 7 cm, belong to RaC', AcA, and partly to ThC' particles which have been slowed down in the layer of the test material.

The number of α-particles with a path length between 5.8 and 7 cm (n_2) is determined by the following relationships:

$$n_2 = n - n_1 = 0{,}663\frac{N_{Th}}{4}\,k\,(8{,}57-5{,}8) + \frac{N_V}{4}\,k\,(6{,}91-5{,}8) + \frac{N_V}{4}\,k\cdot 0{,}04\,(6{,}46-5{,}8) - 0{,}663\times$$

$$\times\frac{N_{Th}}{4}k\,(8{,}57-7);\quad \text{or}\quad n_2 = 0{,}663\frac{N_{Th}}{4}\,k\cdot 2{,}77 + \frac{N_V}{4}\,k\cdot 1{,}11 + 0{,}04\frac{N_V}{4}k\cdot 0{,}66 - 0{,}663\frac{N_{Th}}{4}k\cdot 1{,}57 \qquad (4)$$

By dividing equation (4) by equation (2) it is possible to find the relationship

$$\frac{n_2}{n_1} = 0{,}8 + 1{,}1\frac{N_V}{N_{Th}}\,. \qquad (5)$$

By substituting the value $N_V = 1.2\cdot 10^4\, C_V . d$ and $N_{TH} = 0.4\cdot 10^4\, C_{TH} . d$ where C_V, C_{TH} are the concentrations of uranium and thorium, and d is the density of the material, we find the ratio of the concentration of thorium to that of uranium

$$\frac{C_{Th}}{C_V} = \frac{3{,}3}{n_2/n_1 - 0{,}8}\,. \qquad (6)$$

Formula (6) makes it possible to calculate the relative content of uranium and thorium.

In the present article, which is based on Curie's calculations [9], the ratio of thorium to uranium in minerals and rocks was determined by a photographic method. It has been demonstrated experimentally that it is possible to use photoemulsions for carrying out quantitative measurements. The accuracy of measurements by the photographic method is also evaluated.

MEASUREMENT TECHNIQUE

The accuracy of calculations based on formula (6) depends on the numbers n_1 and n_2. The measurements are most accurate when the number of α-particles recorded is fairly large. For this it is possible to confine oneself to measuring the path lengths for particles which exhibit a small slope to the emulsion surface. This limitation does not affect the ratio n_2/n_1, and, consequently does not affect C_{TH}/C_U. This assumption will only be justified when the value of the slope taken is accurately established.

Measurements of path lengths with large slopes to the emulsion surface (greater than 3°), present considerable difficulties on account of the errors in measuring the depth of the track and the shrinkage factor.

For a limited number of particles measurements were made of track lengths with slopes of up to 25° to the emulsion surface.

The accuracy of measurements of the ratio of thorium to uranium drops somewhat in cases where there is an uneven distribution of the radioelements in the test samples of rock, since, in such cases, during preparation of sections only part of the grain may be captured. Errors which arise during measurement of the track lengths of long-path α-particles in the emulsion also affect the accuracy of the measurements.

The track lengths of RaC' α-particles were determined by two independent methods. The first method was based on determination of the length by the contact method. For this purpose, a transparent section 30-40μ thick, as well as a thin layer of powder 0.5-1 μ thick (0.5 mg/cm²), were prepared from the same sample, the powder being deposited on a backing by means of a precipitation method. In order to prepare the thin layer of powder, a small amount of the uraninite was ground up with a volatile organic liquid (chloroform, alcohol, etc) and then deposited on the plate weighed beforehand. After drying, the exact weight of the powder per unit area of the surface was determined. By preparing a fine layer of powder, it is possible to achieve minimum absorption of α-particle in the radioactive material itself. The samples prepared in this way were combined with a photographic plate, which was then chemically treated and examined under the microscope. The maximum track length found for RaC' α-particles in a Type A-2 No. 2492 emulsion was 40.3 μ.

The second method of determining the path length of RaC' particles was the following. Uraninite powder together with the photographic plate were placed in a hermetically sealed cell, so that only atoms of radon and of its breakdown products could fall on the plate. After the appropriate exposure and chemical treatment, two-ray "stars" appear on the photographic plate. The path length of RaC' α-particles proved to be 40.3 μ in this case also.

Thus, for determination of the number of tracks n_1 and n_2, we assumed that particles with a path length of more than 40.3μ in the emulsion belong only to ThC', while particles having path lengths between 40.3 μ and 33.6 μ belong to RaC' and AcA.

The thick-layer photoplate method based on calculating long-path α-particles makes it possible to establish the thorium-uranium ratio for inclusions with a cross section of up to 0.1 mm². The study of the radioactivity of such small inclusions is very difficult by the usual radiochemical methods.

Thus the photographic method allows one to establish not only the spatial distribution of activity in a given mineral, but also makes it possible to investigate the relative content of uranium and thorium in separate parts of the test object.

EXPERIMENTAL RESULTS

Twenty radioactive minerals and ores were taken for the determination of the relative content of uranium and thorium. Transparent sections 30-40 μ thick without a cover glass were prepared from these samples, and these sections were combined with the photographic plate. After the necessary exposure, the plates were developed and examined under the microscope at a magnification of × 900. Exposure time was chosen in accordance with the activity of the sample, so that the total number of α-particles in one field of view of the microscope did not exceed 30-40, since examination of the plates is difficult when a greater number of particles is involved.

In Table 1 is given the results of measurements of the thorium-uranium ratio, and also a comparison of the results of the photographic method with those obtained by chemical and radiochemical analysis Results obtained by the photographic method are in good agreement with those of chemical and radiochemical analysis.

TABLE 1

Thorium-Uranium Ratios in Minerals and Ores

Designation of the minerals and ores, and their indices	Exposure time of the photographic plates	Area observed, cm	Measurements obtained by the photo.method				Thorium: uranium ratio by the photographic method	Thorium: uranium ratio by the chemical and radiochemichal analysis	Deviation of photographic from chemical and radiochemical results
			Total No. of α-particles measured	n_1	n_2	$\frac{n_2}{n_1}$			
Pitchblende No.5	35 min	0,8	212	—	212	∞	0	0	0
Uraninite 1S	35 .	0,6	131	—	131	∞	0	0	0
Black uranium silicate 1/19	46 .	1,5	264	1	263	263	0,012	0	+0,012
Radioactive mineral 7s	1 ч. 49 .	1,3	242	1	241	241	0,013	0	+0,013
Pitchblende 1/8	48 .	1,5	318	1	317	317	0,01	0	+0,01
Uraninite partially replaced by pitchblende 23/10	55 .	1,3	289	2	287	143,5	0,023	0,025	—0,002
Uraninite and the pitchblende which replaces it 25/4	30 .	3,2	605	11	594	54	0,06	0,004	+0,056
Branerite V-8	1 ч. 08 .	2,1	455	12	443	37,0	0,09	0,08	+0,01
Elsvortite V-3	5 . 10 .	3,2	567	40	527	13,1	0,26	0,23	+0,03
Euxenite E-20	5 . 40 .	1,2	279	37	242	6,54	0,58	0,61	—0,03
Blomstrandite V-6	6 .	2,5	417	102	315	3,08	1,44	1,44	0
Radioactive mineral 33/a	2 . 05 .	1,6	400	105	295	2,8	1,65	1.63	+0,02
Manganese ferritorite V-10	5 . 40 .	2,0	432	174	258	1,48	4,85	5,64	−0,79
Radioactive mineral No.700	2 . 55 .	1,5	331	128	203	1,58	4,23	4,42	—0.19
Ferritorite	2 . 50 .	2,4	506	212	294	1,38	5,69	5,47	+0,22
Actyusite A	5 . 40 .	2,5	476	192	284	1,47	4,9	>1	—
Ferritorite V-2	2 . 50 .	2,0	411	193	218	1,12	10,3	9,17	+1,13
Auerlite V-7	1 . 30 .	2,3	496	238	258	1,08	11,77	14,42	− 2,65
Auerlite No. 100	2 . 40 .	1,5	378	178	200	1,12	10,3	11,96	−1,66
Radioactive mineral F-11	2 . 10 .	3,2	786	366	420	1,14	9,70	—	—

The study of the radioactive minerals and ores can be divided into three groups, depending on the thorium-uranium ratio. To the first group belong samples with the indices No. 5, 1S, 4/19, 7S, 1/8, and 23/10 (Table 1), which either do not contain any thorium at all or only contain it in negligible amounts. To the second group belong the minerals and ores with the indices V-8, 25/4, V-3, E-20, V-6, and 33/A, which contain appreciable amounts of thorium as well as uranium. For these samples the thorium-uranium ratio, according to the chemical analysis, varies within the limits 0.04 to 1.63. The third group consists of the radioactive minerals and ores with the indices V-10, No. 700, 28/2, A, V-2, V-7, No. 100, and F-11, for which the ratio of thorium to uranium is greater than 4.

When thorium is absent in the test material, the thorium-uranium ratio should be equal to zero. This position is confirmed in the case of samples of pitchblende with index 5 and uraninite with the index 1S, which, according to the results of chemical analysis did not contain thorium. Thorium could not be detected in these samples by the photographic method either. We were unable to detect a single trace of a ThC' α-particle in a transparent section from the pitchblende and uraninite, the area being equal to 0.7 cm^2. The remaining minerals and ores of the first group investigated, apparently contain thorium, but in very small amounts. For example, for the samples of black silicate radioactive mineral with index 7S, and pitchblende with index 1/8 only one α-particle was found in each case, while in the case of the uraninite partially substituted by pitchblende, two ThC α-particles were found and 200 and 300 RaC' and AcA α-particles, respectively. The thorium-uranium ratio for these minerals, according to our results is very low. The deviation of the results given by the photographic method from those obtained by chemical analysis lies within the limits of experimental error.

From the results given it is clear that photographic plates can be successfully used for determining the thorium-uranium ratio in minerals and ores. The accuracy of the measurements increases in the case of minerals which keep well, when the radioelements in them are distributed uniformly. When the radioelements are distributed unevenly, it is necessary to accumulate a large amount of statistical data in order to assess the mean value of the thorium to uranium ratio.

The Error in the Determination of the Thorium-Uranium Ratio, and the Sensitivity of the Photographic Method

The error in the determination of the amount of a radioelement on the basis of a count of the number of t traces in an emulsion, is basically determined by the statistical nature of radioactive fission, and by the variation in the number of background traces of α-particles arising as a result of radioactive contamination of the photographic emulsion and the surrounding atmosphere. Accordingly, the error in the measurement of the thorium to uranium ratio will be smaller the larger the number of long-track α-particles from the test material, and the smaller the variation in background tracks.

The statistical errors in the measurement of the thorium-uranium ratio fot the materials tested with a mean value for the thorium-uranium ratio ($C_{TH}/C_U > 3$) lies within the limits 1 to 10%. For samples with a thorium-uranium ratio $C_{TH}/C_U > 3$, the error increases to 20-30%, since in this case, the ratio n_2/n_1 decreases strongly. For the samples with indices V-7, No. 100, and V-2, the statistical error exceeds the indicated value, this can be explained by the large number of ThC' α-particles.

The maximum relative deviation of the results of the photographic method from those of chemical and radiochemical analysis lies within the limits 15 to 20%.

For the quantitative determination of the radio element content of rocks it is necessary to increase the exposure time to one month and more. In addition, the exposure time cannot be made unlimited because of the presence of radioactive contamination in the emulsion itself, and in the glass, and surrounding atmosphere, and also because of the phenomenon of regression of the latent image of the particle tracks. We have shown that the effect of regression can be lowered by placing the plate which is being exposed together with the object in a cell containing nitrogen [10].

The effect of radioactive contamination in freshly prepared photographic plates is not very great. The number of background tracks found on 1 cm^2 of the surface of type A-2, No. 2492 emulsion one month after preparation of the emulsion was approximately 40, this is equivalent to 10^{-7} % U, while after three months this number increased to approximately 100 particles per cm^2. It should be pointed out that tracks of particles arising from the lower layers of the emulsion, or from the glass, are readily distinguished from the tracks of α-particles falling into the emulsion from the air. Moreover, the background tracks are distributed more or less uniformly in the emulsion. Accordingly, their effect can be taken into account by using control plates.

In old photographic emulsions which have been kept for five-six months and longer, the effect of background tracks is considerable (about 220 per cm^2). In such cases, in order to remove the background tracks from the emulsion, the photographic plates are kept for 15 hours in a thermostat in an atmosphere saturated with water vapor at 35°, i.e. the background tracks are subjected to artificial regression. By this means α-particle tracks are almost completely removed from the surface layer of the emulsion and only some of them are preserved in its lower layers. From what has been said above it follows that by observing certain conditions (using fresh photographic plates, placing the plates in a nitrogen atmosphere, and removing the background by keeping the plates in an atmosphere saturated with water vapor, etc.) it is possible to extend the exposure time to several months, and in this way it becomes possible to carry out determinations of the activity of objects with a very low content of radioactive elements. Moreover, the photographic method can be used for studying the thorium-uranium ratio in minerals, where thorium is contained in insignificant amounts. In such cases it is difficult to measure the thorium by the emanation method because of the large influence exerted by actinon. For relatively high values of the C_{TH}/C_U ratio the presence of actinon has hardly any effect at all on the accuracy of measurements by the emanation method.

One of the drawbacks of the photographic method is the complications involved; these are the reasons which hinder its use under field conditions. All the same, when a succession of tests have to be carried out, and where detailed results are required, the photographic method, in our view, remains unreplaceable.

The limiting sensitivity of the photographic method is limited by the α-radiation of radioelements present as impurites in the emulsion, glass backing, and atmosphere. In order to take these effects into account control plates are used; by means of these plates it is possible to determine the number of background tracks on 1 cm^2, and, accordingly, corrections can be applied for them.

When freshly prepared photographic plates are used the sensitivity of the method can be increased to a content of $5 \cdot 10^{-4}$% U.

Measurements in which the background is taken into account and exposure is carried on for two months, makes it possible to carry out determination of the radioactivity down to $5 \cdot 10^{-4}$% U. In order to determine the thorium-uranium ratio the activity should be much higher, of the order of $5 \cdot 10^{-3}$% U.

TABLE 2

Thorium-Uranium Ratio in Mineral Inclusions

Mineral	No. of inclusion	Dimensions of the radioactive inclusions, mm^2	n_1	n_2	$\frac{n_2}{n_1}$	Error in determination of n_2/n_1, %	Mean value of C_{Th}/C_U	Limits of the variations in C_{Th}/C_U (from—to)
Auerlite	1	3,25	52	119	2,3	22,4	2,2	1,1—3,3
	2	1,61	26	47	1,8	34,1	3,3	2,0—8,2
	3	0,94	40	34	0,85	27,6	66,0	11,8—negative number
	4	1,41	44	38	0,86	31,2	55,0	10,3—negative number
	5	0,88	41	25	0,61	35,6	negative number	165,0—negative number
Actyusite	1	0,12	22	41	2,0	36,0	2,7	1,2—6,7
	2	0.19	0	87	—	10	0	—
	3	0,15	19	47	2,4	36	2,0	1,4—4,4
	4	0,27	39	33	0,84	35	82,5	10.0—negative number
	5	0,13	32	28	0,87	37	47,1	8,4—negative number

Variation of the Thorium-Uranium Ratio in the Minerals Auerlite and Actyusite.

During determination of the thorium-uranium ratio in the minerals auerlite and actyusite, variations in the value of the ratio C_{TH}/C_U were detected in grains of these minerals. These minerals were found in lumps of rock in the form of fine grains with dimensions ranging from a few microns to 1-3 mm. In order to demonstrate that there is an actual variation in the thorium-uranium ratio in the grains of these minerals, we removed several grains from each mineral and determined the thorium-uranium ratio for each of them. In order to increase the accuracy repreated determinations were carried out of the thorium-uranium ratio for the same grains.

The mean value of four repeated determinations for the two minerals is given in Table 2. The table also includes the size of the grains, and the error in measuring n_2/n_1 and C_{TH}/C_U. The grain size was determined by comparison the section of the sample with the impression on a photographic plate, which was obtained by long exposures. From the mean values given in Table 2 it is clear that the ratio of thorium to uranium for the grains examined varies within the very wide limits of 2-3 to infinity.

The variations in the values of the thorium-uranium ratio for the grains of the minerals indicated lie outside the limits of experimental error. The negative value of C_{TH}/C_U, calculated by means of formula (6) signifies excess ThC' α-particles. This can be explained by the specific conditions of the emanation, or by experimental error. These values are indicated as negative values in the table. Nevertheless, the variation of the mean thorium-uranium ratio for the grains of the minerals indicated is so large, that, it presumably indicates a complex mineral composition for the "accessories", among which are included mainly uranium and thori minerals.

During a study of the mineral actyusite it was established that individual grains of this material did not contain any thorium.

Thus the thick-layer photographic plate method which is based on calculating the number of long-track α-particles, permits the establishment of the thorium-uranium ratio for inclusions with a cross section down to 0.1 mm^2 and having a weight of the order of 0.3 mg. Studies of the radioactivity of such small inclusions are difficult to undertake by the usual radiochemical methods. Thus, the photographic method permits one,not only to establish the spatial distribution of activity in a given mineral, but also gives the possibility of examining the relative thorium and uranium contents of separate parts of the test material.

In conclusion we should like to thank V. I. Baranov and A. I. Turarinov for discussions on the work and for valuable advice.

SUMMARY

It has been experimentally demonstrated that it is possible to use the photographic emulsion method for determining the relative content of thorium and uranium in minerals and ores. Measurement of the thorium-uranium ratio for $C_{TH}/C_U > 3$ can be carried out with an accuracy of 10-15% . The maximum relative experimental error for $C_{TH}/C_U > 10$ %, does not exceed 20%

The photographic plate method is applicable to the determination of the thorium-uranium ratio in separate microinclusions or grains whose dimensions are about 0.1 mm^2, corresponding to a weight of 0.3 mg. The variations in the thorium-uranium ratio found in microinclusions is a consequence of the fact that grains of the minerals contain uranium and thorium in very different amounts.

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SPECTROGRAPHIC DETERMINATION OF TIN, ZINC, CADMIUM, ANTIMONY, LEAD, AND ARSENIC IN NATURAL WATERS

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With the introduction of hydrochemical methods into the techniques used during the search for ore deposits, analytical methods of high sensitivity are necessary which will enable the content of ore elements in natural waters to be determined at concentrations of these elements of $1 \cdot 10^{-8} - 1 \cdot 10^{-4}$ g/liter. In the first instance use was made of semiquantitative spectrographic analysis of the dry residues obtained from natural waters, this method permitted simultaneous determinations of 35-40 hydrogenic elements [1]. Having obtained the dry residues by evaporating 200-500 ml of water with an average mineral content (of the order of 100 mg/liter), it has been found possible to determine most of the elements with a sensitivity of $n \cdot 10^{-3}$% of the weight of the dry residue, or $n \cdot 10^{-6}$ g/liter.

This method has been widely used for studying the content of micro elements in natural waters from polymetallic deposits. Tin, cadmium, antimony, and arsenic have been detected in a comparatively small number of samples by this method [2]. These results can be explained either by the weak migration capacity of the elements indicated, or by the fact that the sensitivity of the method is not high enough. Accordingly, in order to get a final solution to the question, it was necessary to develop a more sensitive analytical method.

The most important elements to determine were tin, zinc, cadmium, antimony, lead, and arsenic, since an increased content of these elements may serve as an indication of polymetallic deposits.

A small number of papers have been published on the question of the spectrographic analysis of dry residues from natural waters [1, 3, 4]. The most well known is the use of combined spectrochemical methods based on preliminary chemical isolation of the elements to be determined, followed by spectrographic analysis of the concentrates [5-10]. Since the possibilities of a direct spectrographic analysis of dry residues are still far from being exhausted, the first part of the work described here was devoted to the quantitative spectrographic determination of tin, zinc, cadmium, antimony, lead, and arsenic directly in the dry residues from natural waters with a low mineral content.

For test materials with variable bulk composition, dry residues being a case in point, the results of spectrographic determinations depend on the composition of the samples [11]. In order to eliminate the effect of the anions on the line intensity of the test elements, the dry residues were converted into the sulfates by treatment with sulfuric acid. In order to study the effect of calcium, magnesium, and sodium, the concentration of which in natural waters varies considerably, synthetic mixtures of the sulfates of these elements were made up, the proportions of the various elements being varied within the mixtures, while the mixtures also contained small amounts of the oxides of the test elements. Evaporation curves (Fig. 1) and calibration curves (Fig. 2) were constructed; an a.c. arc operating at 16 amps was used.

It is clear from Figs. 1 and 2 that the evaporation and calibration curves for all the test elements and the base elements do not coincide with each other; thus the character of the passage of all the impurities to be determined into the arc depends on the composition of the sample.

In order to lower the effect of the bulk composition of the dry residues on the line intensities of the test

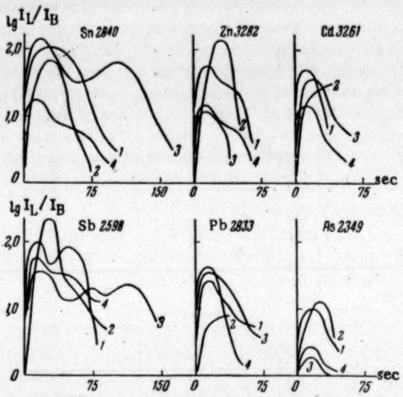

Fig. 1. Variations in the shape of the evaporation curves for Sn, Zn, Cd, Sb, Pb, and As with the main elements in the dry residues:
1) Base $CaSO_4 \cdot 2H_2O$; 2) Base-$MgSO_4 \cdot 7H_2O$; 3) base-Na_2SO_4; 4) base- a mixture of $CaSO_4 \cdot 2H_2O + MgSO_4 \cdot 7H_2O + Na_2SO_4$, consisting of equal parts by weight of the salts indicated; a.c. arc operating at 16 amp.

elements, we diluted the samples with a buffer mixture. The composition of the buffer mixture was chosen experimentally, the aim being to stabilize the evaporation conditions of the samples and the temperature of the arc flame, whatever the composition of the dry residue. The best results, which ensured the possibility of determining all six elements on one sample, were obtained on using the following buffer mixture: 50% NH_4HPO_4 16.7% $CaSO_4 \cdot 2H_2O$, 16.7% $MgSO_4 \cdot 7H_2O$, 16.6% Na_2SO_4. One part by weight of the sample was mixed with two parts by weight of the buffer mixture. In this way the contents of the main components of the mixture were levelled out in the mixtures obtained from original samples differing in composition. The addition of the disubstituted ammonium phosphate enhanced the fractional evaporation of the elements, so that the sensitivity of the determination increased.

It was established subsequently, that in order to increase the accuracy of quantitative analysis, it is advisable, in addition, to introduce an internal standard into the samples and standard mixtures. The internal standard used was germanium, the presence of which in natural waters is very unlikely (it can only be detected in very acid thermal waters having a pH of 1-2 [12]). Germanium was added to the buffer mixture in the form of germanium dioxide (0.035% GeO_2 on the weight of the mixture).

The evaporation curves show that germanium passes into the a.c. carbon arc in an identical manner to tin, zinc, and the other test elements. The calibration curves for the case where the internal standard is germanium, show that the relative intensity of the lines of the test elements in such cases, is also independent of the ratio of the calcium, magnesium, and sodium concentrations in the original samples.

In the dry residues from carbonate waters with a low mineral content, aluminum, iron, and manganese are present (on the average, 0.5% of aluminum, and 0.1% each of iron and manganese). Observations showed that the presence of these affects the relative intensity of the lines of tin, zinc, cadmium, arsenic, antimony, and lead. The experimental error thereby introduced was eliminated by using standard powders identical to the test samples with respect to their content of aluminum, iron, and manganese.

Synthetic standards were used for the analysis. The base for the standards was a mixture containing 31.00% $CaSO_4 \cdot 2H_2O$, 31.00% $MgSO_4 \cdot 7H_2O$, 30.90% Na_2SO_4, 0.15% Fe_2O_3, 0.28% $MnSO_4$, 6.67% $Al_2(SO_4)_3 \cdot 18H_2O$. The iron, manganese, and aluminum contents of this mixture, expressed as the metal, were 0.1, 0.1, and 0.5% wt. respectively. The composition used for the base of the standards is the nearest approximation to the mean content of calcium, magnesium, sodium, iron, manganese, and aluminum in the dry residues from carbonate waters with a low mineral content. By adding the oxides of the test elements to this base mixture, a primary standard containing 0.1% each of tin, zinc, cadmium, antimony, lead, and arsenic was obtained.. Standards with lower contents of the elements right down to 0.0001%, were prepared by successive mixing of one part of the primary standard with two parts by weight of the base.

Further, both the standards and samples — the dry residues from natural waters — were mixed with a buffer mixture of the composition indicated above, containing germanium as the internal standard; to two parts by weight of the buffer mixture was added one part by weight of the test sample (or standard). Mixing of all materials, both during the preparation of standard powders, and during the dilution of samples with the buffer mixture, was carried out by careful grinding in an agate mortar in the presence of alcohol.

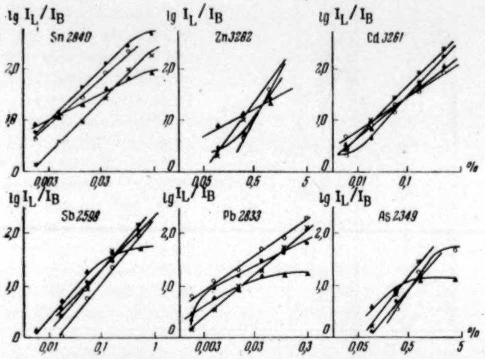

Fig. 2. Displacement of the calibration curves for Sn, Zn, Cd, Sb, Pb, and As caused by changes in the composition of the base of the dry residue.
x) Base - $CaSO_4 \cdot 2H_2O$; △) base - $MgSO_4 \cdot 7H_2O$; o) base - Na_2SO_4; O) base - a mixture of $CaSO_4 \cdot 2H_2O + MgSO_4 \cdot 7H_2O + Na_2SO_4$ consisting of equal parts by weight of the salts indicated. a.c. arc, i = 16 amp, complete burning.

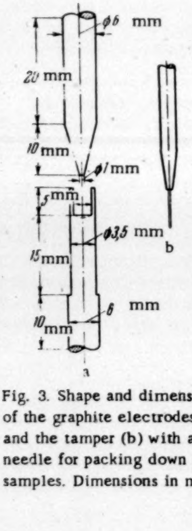

Fig. 3. Shape and dimensions of the graphite electrodes (a), and the tamper (b) with a needle for packing down the samples. Dimensions in mm.

All the materials used were checked beforehand for the absence of the elements to be determined in them.

The mixtures obtained were weighed out on a torsion balance in 15mg portions. Each portion of powder was placed in the canal of the lower graphite electrode and compressed with a special tamper (Fig. 3).

Samples and standards were fired in a vertically arranged 16 amp carbon a.c. arc at a voltage of 220 volts. The arc was supplied from a DG-1 generator with a discharge gap in the arc circuit of 0.45 mm. The distance between the electrodes was kept equal to 2 mm during arc burning. The spectra from two carbons was taken on one place on the photographic plate. Each exposure time was 30 seconds (total exposure was one minute). The duration of arc burning was established on the basis of the evaporation curves.

The spectra were photographed on an ISP-22 quartz spectrograph with a three-lens illuminating system; the slit width of the spectrograph was 0.012 mm; which the plates used were "Spectrographic type " with a sensitivity of not less than 16 GOST units. The plates were developed at 18° for 3 minutes in a high-contrast metol-hydroquinone developer.

The table contains details of the analytical lines used, and also comparative results illustrating the sensitivity of determination under the conditions of the method developed, and under the conditions used for semiquantitative analysis as described in [3].

It should be pointed out that during the determination of low concentrations of elements in dry residues (approximating to the limit of the sensitivity of detection of the elements), the intensity of the lines is comparable in magnitude to the intensity of the background: $I_L = I_{Back.}$ [13, 14]. Accordingly, during measurement of the relative intensity, the background intensity is excluded beforehand from the intensity of the impurity lines and the reference lines. The choice of where to make the measurements of the background on the spectrograms was made on the basis of a method suggested by Filimonov [15, 16]. Experiments which we carried out showed that it is best to measure the background as minimum blackening directly in the neighborhood of the analytical lines. For the lines Sn 2840.0 ; Sb 2598.1; Cd 3261.0; As 2349.8; Ge 2754.6 the background was measured on the short-wave side of the analytical lines, while for the lines Zn 3282.3 and Pb 2833.1 the background was measured on the long wave side of the analytical lines.

Test element	Analytical line, A	Sensitivity of the determination, %		Test element	Analitical line A	Sensitivity of the determination, %	
		By semi-quantitative analysis	By quantitative analysis*			By semi-quantitative analysis	By quantitative analysis *
Tin	2840.0	$1 \cdot 10^{-3}$	$1.3 \cdot 10^{-4}$	Antimony	2598.1	$1 \cdot 10^{-2}$	$1.2 \cdot 10^{-3}$
Zinc	3282.3	$1 \cdot 10^{-1}$	$3.7 \cdot 10^{-3}$	Lead	2833.1	$1 \cdot 10^{-3}$	$4.3 \cdot 10^{-4}$
Cadmium	3261.1	$1 \cdot 10^{-2}$	$1.2 \cdot 10^{-3}$	Arsenic	2349.8	$1 \cdot 10^{-1}$	$3.7 \cdot 10^{-3}$

*The 2754.6 A of the internal standard, germanium, which is common to all the test elements, was used for the quantitative determinations.

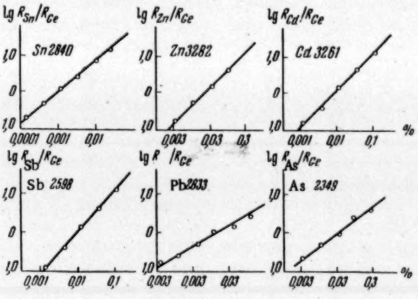

Fig. 4. Calibration curves for the determination of Sn, Zn, Cd, Sb, Pb, and As.

The blackening of the lines and of the background around them was measured on a MF-2 microphotometer. Conversion from blackening to intensity, and elimination of the background intensity $I_{Back.}$ from total intensity of line and background $I_{n + Back.}$ was carried out by means of a calculator based on the characteristic curve of the photographic plate.

The calibration curves were constructed within the coordinates log $R_{El.}/R_{Ge}$; log C, where $R_{El.} = I_{El.}/I_{Back.\,El}$ is the ratio of the line intensity of the test element to the background intensity near this line, and $R_{Ge} = I_{Ge}/I_{Back.\,Ge}$ is the ratio of the line intensity of the internal standard, germanium, to the background intensity near this line, and C is the concentration of the test element.

For a single determination, one spectrogram of the sample was used in conjunction with a calibration curve, each point of which was obtained by meaning the results of the photometric measurements of one spectrogram of each standard.

On the basis of 170 control analysis of mixtures of the sulfates of calcium, magnesium, and sodium with known contents of the test elements, it was established that the mean probable error of a determination amounts to ± 12% relative.

The technique developed permits quantitative determination of the test elements in the following concentration ranges: tin from 0.00013 to 0.1%; zinc from 0.0037 to 0.1%; cadmium from 0.0012 to 0.1%; antimony from 0.0012 to 0.1%; lead from 0.0004 to 0.1%; and arsenic from 0.0037 to 0.1%.

It should be possible to determine copper. Where this is done however, contamination of the spectrographically pure carbon electrodes by copper should be borne in mind.

Using the method developed, tin, zinc, cadmium, antimony, lead, and arsenic were quantitatively determined in 155 dry residues from carbonate waters with a low mineral content. The enhanced sensitivity of the method made it possible to detect tin in 143 cases as against 99 found previously by semiquantitative analysis, zinc was found in 87 instead of 37, lead in 154 instead of 91, antimony in 15 instead of 1, and arsenic in 20 instead of 10. Cadmium was not detected in any of the dry residues tested.

SUMMARY

A method has been developed for the quantitative spectrographic determination of $1.3 \cdot 10^{-4} - 1 \cdot 10^{-1}\%$ of tin, $4.3 \cdot 10^{-4} - 1 \cdot 10^{-1}\%$ of lead, $1.2 \cdot 10^{-3} - 1 \cdot 10^{-1}\%$ antimony and cadmium, and $3.7 \cdot 10^{-3} - 1 \cdot 10^{-1}\%$ of zinc and arsenic in the dry residues obtained from natural waters with a low mineral content; the probable error of a single determination is ± 12% relative. Determination of copper is possible but contamination of the spectrographically pure carbon electrodes by the copper must be borne in mind.

By means of the method developed, tin, zinc, antimony, lead, and arsenic have been determined in 155 dry residues from carbonate waters with a low mineral content. Cadmium was not detected.

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ANALYTICAL APPLICATIONS OF 8-MERCAPTOQUINOLINE (THIOOXINE) AND ITS DERIVATIVES

COMMUNICATION 4. THE PHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF MANGANESE *

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The published literature on photometric methods of determining manganese is comparatively poor. In the first instance mention should be made of the different variants of the general method of determining manganese, based on its oxidation to the permanganate ion [1-7]. This method is very specific and allows determination of manganese in most natural objects without its preliminary separation from other foreign elements. Appreciable concentrations of colored ions and chlorides interfere. In many instance, however, the sensitivity of the reaction is insufficient for determination of traces of manganese without its preliminary concentration.

Divalent manganese ions in alkaline solution react with formaldoxime to form a reaction product which colors the solution brown [8-9]. Iron and other elements interfere. Schroder has suggested a photometric method for the determination of trivalent manganese ions which are formed during the oxidation of Mn^{2+} in a medium of phosphoric and perchloric acids [10]. It has also been suggested that manganese be oxidized to the trivalent state by means of bromate in a medium of 8 N N_2SO_4 [11]. Using this method it is possible to determine from 2 to 70 mg of Mn in 100 ml of solution photometrically. Specker, Hartkamp, and Kuchtner [12] have suggested photometric determination of the diethyldithiocarbamate of trivalent manganese. Lukina, Osetrova, Karanovich, and Chernitskaya [13] have studied salicylal-o-aminophenol as a reagent for manganese. The mechanism of the reaction of Mn with this reagent is catalytic. The authors have shown that it is possible to determine manganese in the presence of μgram amounts of certain foreign elements. It has been suggested that manganese can be determined by means of the violet color of the complex pyrophosphatomanganic acid, but the sensitivity of this reaction is low [14]. A number of other methods based on oxidation of organic compounds by the permanganate ion have not found practical application. Reactions of this type are very sensitive but not very specific[7].

Compared with a number of other elements, divalent manganese does not display a strong chromophoric action, accordingly few sensitive reactions are known for this element which are based on the formation of intensely colored complex compounds with organic reagents. In this connection the thiooxine reaction is of considerable value for the photometric determination of manganese.

In alkaline and ammoniacal solutions (in the presence of tartrates and citrates) divalent manganese reacts with thiooxine to form a brown colored inner-complex salt. This can be prepared in a pure form by adding a solution (1:100) of manganese chloride dropwise and with stirring to excess of a freshly prepared and filtered solution of potassium thiooxinate containing sodium tartrate. The brown, amorphous precipitate of the manganese complex is slowly filtered off under suction, washed several times with water and then with alcohol and dried in a vacuum oven at room temperature.

Found % Mn 14.55; S 16.91; N 7.55 $Mn(C_9H_6NS)_2$. Calculated % Mn 14.66; S 17.06; N 7.46.

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*Communication 3, see J. Anal. Chem. 13, 643 (1958).

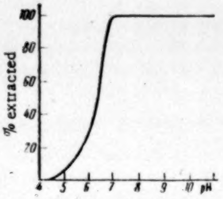
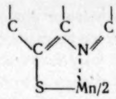


Fig. 1. Extractability of manganese thiooxinate as a function of the pH of the medium.

Manganese thiooxinate is insoluble in water, but is readily soluble in most organic solvents to give solutions which are colored an intense brown. It is sparingly soluble in carbon disulfide and carbon tetrachloride. It is insoluble in aliphatic hydrocarbons. Extracts of manganese thiooxinate in toluene, benzene, chlorobenzene, and xylene, are stable for two days. On keeping for a longer time, the extinction of the extracts gradually decreases. Solutions of manganese thiooxinate in chloroform and bromoform are less stable (presumably, because of the enhanced photochemical sensitivity of these solvents). Chloroform solutions of manganese thiooxinate are destroyed in a matter of minutes under the action of short-wave ultraviolet radiation.

Because of the instability of MnS in acid solutions, and because of the incapacity of manganese to form stable coordination bonds with nitrogen, one could hardly expect formation of a highly stable five membered ring with the following group



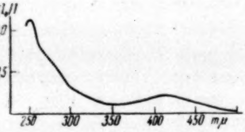


Fig. 2. Absorption spectrum of a 0.000033 M solution of manganese thiooxinate in chloroform.

Actually, as is evident from Fig. 1, manganese thiooxinate is only stable in alkaline solutions and is extracted at pH > 7.

The limits within which manganese thiooxinate can be extracted were investigated as follows. 40 γ of Mn was added to a buffer mixture with a certain pH contained in a separating funnel. The solution was made up to 50 ml with the same buffer, and 2 ml of a 3% alcoholic solution of thiooxine dihydrate $C_9H_6NSH \cdot 2H_2O$ added; the manganese thioxoinate was then extracted with 10 ml of toluene. The amount of manganese was determined by means of a calibration curve.

Manganese thiooxinate prepared as described above was used for taking the absorption spectrum. The spectrum was registered on a SF-4 spectrophotometer, the chloroform solution of the manganese complex being frequently changed because of the destructive effect of the ultraviolet radiation on manganese thiooxinate.

As is evident from Fig. 2, the light absorption curve for manganese thiooxinate has two maxima: at $\lambda_1 = 250$ mμ (molar extinction coefficient $\epsilon_1 = 34{,}000$) and at $\lambda_2 = 413$ mμ (molar extinction coefficient ϵ_2 about 7,000).

Conformity to Beer's law was studied by the same method, using the same sequence of operations as those described for studying the extractability of manganese thiooxinate as a function of the pH of the solution.

As is evident from Fig. 3, solutions of manganese thiooxinate in carbon tetrachloride conform to Beer's law down to 4 γ in 1 ml of CCl_4.

Thiooxine in aqueous solutions only reacts with those elements which form sulfides which are stable to the action of water. The alkali and alkaline-earth metals, as well as Al, Cr, Zr, Th, Ti, La etc, even in appreciable concentrations, do not interfere with manganese determination.

In view of the fact that the thioxine reaction for manganese is carried out in an alkaline medium, its specificity (without resorting to masking complexing agents) is low, since, in alkaline solutions, most elements which form sulfides which are stable to the action of water react with thiooxine. The only exceptions are those elements which exist in alkaline solutions in the form of very stable anions. In the given instance, this is mainly true of molybdates, tungstates, and arsenates. Potassium cyanide is used for masking iron, nickel cobalt, palladium, and some other elements in their lower valence states. In the form of their cyanide complexes these metals do not interfere with the determination of manganese. The cyanide complex of manganese has a low stability at pH 10 and interacts with thiooxine to form manganese thiooxinate.

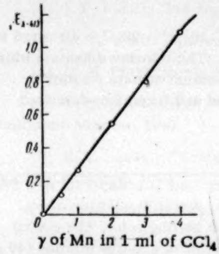


Fig. 3. Conformity to Beer's law of solutions of manganese thiooxinate in carbon tetrachloride (light filter S = 42).

It is very important to complex iron completely as the complex ion $[Fe(CN)_6]^{4-}$, this can only be achieved under very strictly defined conditions. None of the variants of this method of masking iron used by other research workers proved suitable in our case. Using these variants some of the iron always remained uncomplexed. After numerous experiments we became convinced that in order to bind iron completely as the complex $[Fe(CN)_6]^{4-}$ two conditions must be fulfilled: 1) iron must be completely reduced to the divalent state, ascorbic acid is the best reducing agent for this purpose (other organic reducing agents proved to be insufficiently active); 2) complexing of the iron as the cyanide complex should be carried out at a pH of 9.5-10.5. At lower or higher pH values, complexing of iron is incomplete. Silver and gold in alkaline solutions are reduced to the metals and do not interfere with the determination of gamma amounts of manganese. Of the platinum metals, the effect of Pt, Pd, Ir, and Os was studied. Platinum in amounts of 20 mg, under the conditions of the method developed, colored the extract an intense blue. The behavior of smaller amounts of Pt (1-2 mg) was not studied.

Palladium, iridium, and osmium in milligram amounts do not interfere with manganese determination. Lead, zinc, cadmium, thallium, vanadium, and tin should be absent.

Determination of Manganese in the Presence of Various Elements (taking 5 γ Mn)

Foreign element (Me), mg	Ratio Mn : Me	Mn found, γ	Foreign element (Me), mg	Ratio Mn : Me	Mn found, γ
Fe^{III}—5	1 : 1000	5,0	As^{V}—10	1 : 2000	4,8
Cu^{II}—3	1 : 600	4,8	Hg^{II}—0,05	1 : 10	5,1
Ni^{II}—15	1 : 3000	4,7	Ag—10	1 : 2000	4,9
Co^{II}—10	1 : 2000	5,1	Au^{III}—20	1 : 4000	5,2
Pd^{II}—20	1 : 4000	5,1	Os^{VIII}—5	1 : 1000	5,0
Mo^{VI}—30	1 : 6000	5,0	W^{VI}—20	1 : 4000	5,0
Sb^{III}—1	1 : 200	4,9	Re^{VII}—10	1 : 2000	5,1
Bi^{III}—0,02	1 : 4	5,2	Ir^{IV}—15	1 : 3000	5,2

Using a SF-4 spectrophotometer for optical measurements, and using 5 ml of extracting agent for the extraction, it is possible to determine as little as 1.5 γ Mn with satisfactory accuracy. Using 10 ml of extracting agent and a Pulfrich photometer, it is possible to determine 3 γ Mn in 50-100 ml of solution.

Preparation of Reagent Solution.

A solution of thioxine in carbon tetrachloride in which the concentration is 35 mg/liter is used. Such a solution is best prepared by extracting a suspension of thioxine dihydrate with carbon tetrachloride, the suspension having been prepared by neutralization of concentrated aqueous solutions of thioxine salts. When this technique is used, the thioxine passes into the organic solvent layer in the anhydrous state — C_9H_6NSH. From its solution in CCl_4, on shaking water, a considerable amount of the thioxine passes into the aqueous phase in the form of the dihydrate $C_9H_6NSH \cdot 2H_2O$.

Thioxine solutions in CCl_4 have a very weak yellow color and are stable for a minimum of one month. The stability of the solutions is strongly dependent on the purity of the carbon tetrachloride.

a) Preparation of a Solution from Thiooxine Hydrochloride. 4.28 g of thioxine hydrochloride is placed in a 250 ml separating funnel and 10 ml of twice-distilled water added. On shaking, the thioxine hydrochloride first dissolves, and then a thick bright-red crystalline precipitate of thiooxine dihydrate separates out. 100 ml of CCl_4 is added to the separating funnel and the whole thoroughly shaken, most of the red crystals disappear. 3-4 ml of a 10% solution of sodium acetate is then added, and shaking continued for several minutes until the red precipitate has dissolved completely in the CCl_4. The CCl_4 layer which has a yellow color is separated from the aqueous phase and slowly filtered through a plug of cotton wool.

b) From the Potassium Salt of Thiooxine. 5.11 g of potassium thiooxinate $C_9H_6NSK \cdot 2H_2O$ is dissolved in 10 ml of twice-distilled water, and neutralized with 1.5 ml of glacial acetic acid. The thioxine dihydrate which is precipitated is extracted with 100 ml of CCl_4 as described above. 3 ml of 10% sodium acetate solution is added and the extraction continued for several minutes. The CCl_4 layer is removed and filtered as described above.

Analytical Procedure

To 15-20 ml of a weakly acid test solution contained in a 100 ml Erlenmeyer flask is added 2 ml of a 5% solution of ascorbic acid, and the pH of the solution is ad usted to a value of 7-8 by dropwise addition of 5% NaOH solution; 5 ml of 5% KCN solution is then added and the whole heated to the boiling point. The cooled solution is transferred to a separating funnel and the flask rinsed with two 3 ml portions of a buffer solution (46 g $Na_2B_4O_7 \cdot 10H_2O$ and 9 g KOH per liter) and the total volume in the separating funnel made up to 50 ml with the same buffer solution; the pH at this stage should be about 10. 1 ml of the solution of the reagent in CCl_4 is added and the whole shaken vigorously for 1 minute, when 9 ml of pure CCl_4 is added and shaking continued for a further 3 minutes. The extract is allowed to stand and is then transferred to a second separating funnel after carefully separating it from the aqueous phase. Another 3 ml of pure CCl_4 is added to the first separating funnel and the contents shaken up. After the layers have separated, the second extract is combined with the first extract in the second separating funnel, care being taken to prevent any of the aqueous phase from getting into the second funnel.

25-30 ml of water acidified with hydrochloric acid so that the pH is exactly 3, is added to the second funnel and the whole shaken vigorously for 3 minutes. During this process the manganese passes completely into the aqueous phase, while foreign elements accidentally partially extracted during the first extraction remain in the extract. After the layers have separated out, the carbon tetrachloride is rejected, while the aqueous phase is washed with two lots of 5 ml of pure CCl_4.

The aqueous phase is transferred to a 100 ml flask and 2 ml of a 5% ascorbic acid solution added, the pH is adjusted to 7-8 by means of 5% NaOH, and 5 ml of 5% KCN solution added; the mixture is finally heated to the boiling point. The cooled solution is transferred to a separating funnel and the flask rinsed with two lots of 3 ml of the buffer solution mentioned above; the total volume of solution in the separating funnel is made up to 50 ml with the same buffer solution. 1 ml of the carbon tetrachloride solution of the reagent is added and the while vigorously shaken for 1 minute, 9 ml of pure CCl_4 is added and the shaking continued for a further 3 minutes. The manganese thiooxinate extract is separated, and filtered through a cotton wool plug; the solution is measured photometrically at 413 $m\mu$, or by means of a S-42 light filter, and the amount of Mn determined by means of a calibration curve; the latter is constructed using pure solutions of manganese, all the reagents mentioned above being used.

Results obtained by this method are given in the Table.

SUMMARY

1. The interaction of thiooxine with divalent manganese has been studied. Manganese thioxinate $Mn(C_9H_6NS)_2$ is insoluble in water and is readily extracted by most organic solvents to give solutions with an intense brown color.

2 A photometric method has been developed for the determination of small amounts of manganese. In the presence of potassium cyanide, the method permits determination of Mn^{2+} in the presence of considerably greater amounts of many elements (Fe, Cu, Ni, Co, Pd, Mo, Sb, As, Ag, Os, W. Re and Ir).

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ISOTOPIC ANALYSIS OF WATER

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Various methods have been described for the isotopic analysis of water [1-6],*they include optical, mass-spectrometric, and densitometric methods, and those based on the magnetic momenets of the nuclei, etc. We have developed a method for the isotopic analysis of water which is based on isotopic exchange between water and carbon dioxide, and on measurement of the density by a differential pyknometric method. By carrying out the isotopic reaction between water and CO_2 at 50-100 atmospheres and 90° the possibilities of determining the concentration of the heavy isotopes of oxygen in water are extended as compared with other methods, in which this reaction is carried out at atmospheric pressure and room temperature [2-3]. From the decrease in density of water enriched with O^{17} and O^{18}, as a result of a one-stage isotopic exchange reaction with CO_2, it is possible to determine the concentration of the heavy isotopes of oxygen in the original water. By means of several analogous reactions the isotopic composition of the oxygen of water can be readily reduced to its normal compositon.** In the variant we have developed of the differential pyknometric method of determining density*** the effect of variations in the temperature of the thermostat is considerably reduced, this means tha in the case of mass analyses measurement is essentially simplified, and te error of the pyknometric method is decreased ($\pm 10^{-6}$ g/cm^3) in comparison with published results [3].

The dimensionless magnitude $\Delta \rho / \rho_0 = (\rho - \rho_0)/\rho_0$ where ρ is the density of the test water and ρ_0 is the density of the standard water, characterizes the increase in density on increasing the concentration of deuterium and the heavy isotopes of oxygen (O^{18} and O^{17}). Similarily, we designate by $\Delta\rho_D / \rho_0 = (\rho_D - \rho_0)/\rho_0$ and $\Delta\rho_k/\rho_0 = (\rho_k - \rho_0)/\rho_0$ the increase in density of the water following upon an increase in the concentration of deuterium only, or upon an increase in the concentration of the heavy isotopes of oxygen only, respectively (ρ_D is the density of the test water; in which only the deuterium concentration is higher than in the standard water; ρ_k is the density of water in which which only the concentration of the heavy isotopes of oxygen is higher than in the standard water). It is assumed that $\Delta\rho_D/\rho_0$ and $\Delta\rho_k/\rho_0$ are independent. Then it is obvious that $\Delta \rho/\rho_0 = \Delta\rho_D/\rho_0 + \Delta\rho_k/\rho_0$.

ρ_D/ρ_0 and ρ_k/ρ_0 are determined experimentally. On the basis of these results the concentration of deuterium C_D is calculated as well as a certain effective concentration of heavy isotopes of oxygen $C_k \cong c_{18} + 0.5\, c_{17}$.

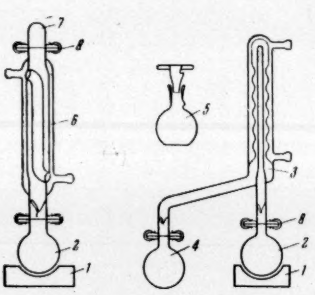

Fig. 1. Flask heater; 2) boiler; 3) vertical straight condenser; 4) condensate receiver; 5) quartz condensate receiver (for the last distillation); 6) reflux condenser; 7) cover; 8) clip.

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*References are only made to reviews and recent original work.

**By normal isotopic composition is meant the isotopic composition of the oxygen in standard water(in our experiments Moscow tap water).

***The first variant of the method described for measuring density was developed and used for controlling technological processes under the leadership of M. I. Kornfel'd in 1944-1945.

Purification of the Water

When the water does not contain appreciable amounts of impurities, in particular organic materials, then it is sufficient to: a) boil the water under reflux for about one hour in the presence of potassium permanganate; b) carry out a three-fold distillation, rejecting the initial and final fractions (10% of the volume of liquid distilled). In such cases, the error in determining the ratio ρ / ρ_0 arising from insufficient purification of the water is considerably less than $1 \cdot 10^{-6}$. When appreciable amounts of organic impurities are present, in addition to the two processes outlined above, the water is preliminarily purified by oxidation of impurities on a catalyst (e.g. cupric oxide) at a temperature of about 700° by a stream of oxygen. * Control measurements showed that the electrical conductivity of the purified water was less than $10^{-5} \text{ohm}^{-1} \text{cm}^{-1}$

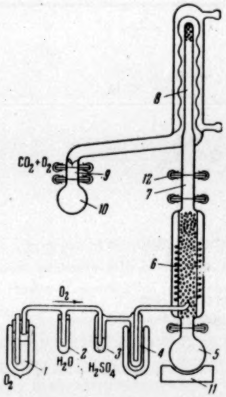

Fig.2. 1)Dewar vessel containing liquid oxygen; 2) pressure limiter; 3) sulfuric acid trap; 4) trap cooled with liquid air; 5) boiler; 6) quartz oven containing the catalyst; 7) connecting joint; 8) condenser; 9) connecting joing with opening; 10) receiver; 11) flask heater; 12) clip.

For low and average concentrations of deuterium the distillation apparatus composed of plane standard ground joints (Fig. 1), is used, this is very convenient for mass analyses. The apparatus used for oxidizing impurities at high temperatures is shown in Fig. 2. Before an analysis the apparatus is freed from traces of water remaining from a previous analysis by purging with hot air.

A quartz apparatus (Fig. 3) is used for purifying water with a high deuterium concentration. During the collection of the first fractions from each distillation, the dropper is placed in position a; when the purified product is being collected the dropper is rotated on the joint into position b. The inner tubes in the first two straight condensers are conical; in operation, the narrow opening (diameter 3 mm) of the preceding condenser is sealed with a drop of water. The assembled apparatus is heated and dried under a vacuum for about one hour. A few ml of the test water is introduced into the flask, and, by heating the apparatus, all this water is pumped off (it is collected in trap 5), i.e. the apparatus is washed with the vapors of the test water. Dried air is let into the apparatus and a few crystals of dry permanganate placed in the flask, the test water is then introduced. The apparatus is connected to the atmosphere through two traps containing liquid air. The water is first boiled under reflux, the cooling is then stopped, and the original fraction which is to be rejected is then distilled to dryness through the remaining flasks of the apparatus into the dropper offshoot, while the middle fraction is distilled into the second flask. Before starting the second distillation the flask with the reflux condenser is cooled (by immersing it in tap water). The second and third distillations are then carried out in the same way, all the three original fractions being collected in the dropper offshoot, while the final fractions remain in the flask-boilers.

The standard water is purified in the same way in the same apparatus as that used for purifying the test water. Prior to filling the pyknometers the purified product and the standard water are kept in quartz vessels.

Calibration of the Pyknometers

Quartz (preferably) or glass pyknometers with a capillary diameter of about 0.1 mm, and 15 mm long were used [3, 7]. Since the density of the water is measured independently twice, and each measurement is carried out in two pyknometers, it is necessary to choose four approximately similar pyknometers. They are annealed until their weights are similar within the sensitivity of the balance.

The pyknometers are first rinsed with water (2-3 ml), dried under vacuum, and then filled. The filler makes it possible to fasten the pyknometer with the funnel either underneath (with the capillary on top) and the

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*After such an operation, only the deuterium concentration can be determined accurately.

cover on top, or vice versa (Fig. 4). Water poured into the pyknometer serves as a lubricant for the conical ground joints of the pyknometers. By successively changing the pressure in the filler, the water is poured into the pyknometers and then degassed under vacuum until no more bubbles are evolved from the pyknometers. If, during this operation, the upper part of the capillary is not filled, then by gentle heating (e.g. in the hand) the water will expand, and the last bubble of air will be expelled from the capillary. That the capillaries are completely full is readily observed in the light. For control, the filled pyknometers are held under suction for a few minutes. In order to pour the water out of the pyknometer, it is necessary to introduce some bubbles of air into it beforehand, and then successively change the pressure in the filler.

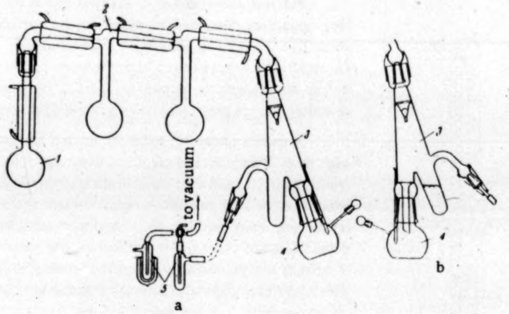

Fig. 3. 1) Distillation flask with a reflux condenser; 2) intermediate boiler with straight condenser; 3) dropper; 4) flask for the purified product; 5) trap with liquid air.

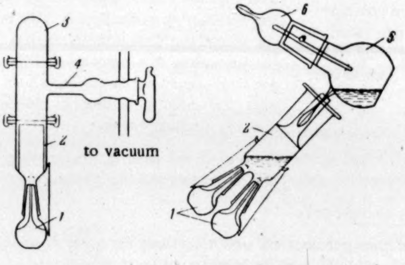

Fig. 4. 1) Pyknometers; 2) filling funnels; 3) cover; 4) filler; 5) quartz for water with high concentrations; 6) cover for it.

The pyknometers filled with standard water are placed in the cradle of a rotating stirrer (rotated by means of a Warren motor at 60 revolutions/minute) in a thermostat, the temperature of which is kept 2-4° above room temperature. The level of the water in the thermostat should be such that the joints of the pyknometers stick out above the surface of the water in the thermostat (about 10 mm). Both pyknometers appear successively in the same places in the thermostat. The difference between the temperatures of both pyknometers wil be, at least, of one order less than the variations in temperature of the thermostat which is readily maintained with an accuracy of ± 0.01° when an ultrathermostat type TS-15 is used. Large pyknometers (25 ml) should be kept in the thermostat for 40 minutes, while small ones (10 ml) should be kept for 30 minutes. During this period the pyknometers acquire the temperature of the thermostat and a drop of water appears on the end of the capillary and dries out gradually. It is essential to ensure that the ends of the capillaries become dry simultaneously. Where necessary a filter paper can be used for removing part of a drop from the end of one of the pyknometers. Both pyknometers are removed simultaneously from the thermostat, and, after 15-20 minutes, wiped with alcohol, and placed on different pans of a balance. The balance used in the course of our work was one with a sensitivity of $\pm 10^{-5}$ g, and capable of handling a maximum load of 50 g. As a rule, one of the pyknometers filled with standard water is heavier than the other. Weights are added to the lighter pyknometer and the balance readings determined.

TABLE 1

$\Delta\rho/\rho_0$ at 25°	Correction	$\Delta\rho/\rho_0$, at 25°	Correction	$\Delta\rho/\rho_0$, at 25°	Correction	$\Delta\rho/\rho_0$, at 25°	Correction
0	0	0,01	0,000080	0,07	0,000230	0,107	0,000008
0,0001	0,000001	0,03	0,000220	0,09	0,000140	0,107720	0
0,001	0,000012	0,05	0,000260	0,1	0,000070		

In order to diminish the effect of variations in the density of air, both pyknometers should have volumes as near as possible to each other (within about 0.5 ml for pyknometers with a volume of about 10 ml and within the limits of about 1 ml for pyknometers with a volume of about 25 ml).

The true weight of the standard water in the volume of the pyknometer at the thermostat temperature is given by: $P - P_1 - P_0$, where P_0 is the true weight of the dry pyknometer, and P_1 is the true weight of the pyknometer plus standard water at the thermostat temperature. Reduction of the weighing results to weights in vacuo is carried out by taking into consideration the density of quartz, water, brass weights and the small weights.

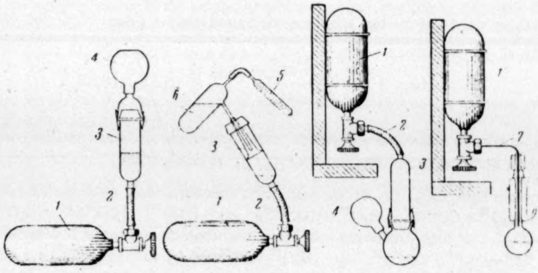

Fig. 5. 1) Reaction vessel; 2) rubber shunt; 3) glass funnel; 4) rubber bulb; 5) trap with P_2O_5; 6) ampoule with two capillary sideshoots for samples with high deuterium concentrations; 7) metal capillary; 8) receiver of the purification apparatus.

Density Determination

The density of the water is calculated from two measurements in different pyknometers. In order to determine the density of the water, one of the pyknometers is filled with standard water, and the second with with test water. They are placed in the thermostat at the same time, and are placed on the balance pans together with the calibration weights in exactly the same way as was done during calibration. Taking into account the balance readings during calibration, the difference is determined between the weights of the test and and standard water P' in the volume of the pyknometer to be filled with test water at the thermostat temperature. The weighing results are reduced to those in vacuo: $\Delta P = \Delta P' - \delta\Delta P'/d$, where δ is the density of the air during weighing, and d is the density of the weights. All the other loads on the balance pans at the moment of determining $\Delta P'$ are not necessary for correcting for the density of the air, since they were used during the calibration. Knowing the true values of ΔP and the weight of the standard water in the volume of the pyknometer P, $\rho/\rho_0 = \Delta P/P$ is found for the test sample.

The isotopic composition of the middle fraction collected differs slightly from that of the original sample, as a result of the removal of the initial and final fractions (10% of the volume of water being distilled). Accordingly, it is necessary to apply corrections which are obtained by means of the Rayleigh formula for the distillation effect – to the results for $\Delta\rho/\rho_0$; these corrections, which are given in Table 1, are only significant at average concentrations.

Determinations of ρ_D/ρ_0 and ρ_k/ρ_0

For separate determination of the increase in density arising from the deuterium $\Delta\rho_D/\rho_0$, and the heavy isotopes of oxygen $\Delta\rho_k/\rho_0$, use is made of the phenomenon of isotopic exchange between the test water and carbon dioxide. A certain amount of carbon dioxide and the test water are introduced into the reaction vessel.* After the time necessary for establishment of isotopic equilibrium has expired, the water is poured out of the vessel.

Having determined the density of the water before the isotopic reaction and after it, and knowing the weight of water and carbon dioxide participating in the reaction, it is possible to determine the value of $\Delta\rho_k/\rho_0$ in the original water [8]:

$$\frac{\Delta\rho_k}{\rho_o} = \left(\alpha_k \frac{M_1 P}{2MP_1} + 1\right)\left(\frac{\Delta\rho}{\rho_o} - \frac{\Delta\rho'}{\rho_o}\right),$$

where $\Delta\rho/\rho_0$ is measured before the reaction; $\Delta\rho'/\rho_0$ is measured after the reaction; P is the weight of the water; P_1 is the weight of carbon dioxide; M is the mean molecular weight of water; M_1 is the mean molecular weight of carbon dioxide; a_k is the partition coefficient between water and carbon dioxide (to the first approximation, on the basis of the O^{18} isotope).

The mean molecular weight of the test water can be calculated by means of the formula

$$M = M_{H_2O} + \frac{M_{D_2O} - M_{H_2O}}{d_{25}^{25} - 1} \cdot \frac{\Delta\rho}{\rho_o} = 18{,}02 + 18{,}68 \cdot \frac{\Delta\rho}{\rho_o},$$

where M_{D_2O} and M_{H_2O} are the molecular weights of 100%, deuterium oxide and standard water respectivley, d_{25}^{25} is the ratio of their densities at 25° (the value of $\Delta\rho/\rho_0$ is taken at 25°).

At 90° for the system $H_2O - CO_2$, i.e. at low deuterium concentrations, when the exchange is determined mainly by the reaction $H_2O^{18} + CO^{16}O^{16} \rightleftharpoons H_2O^{16} + CO^{16}O^{18}$, $\alpha_k = [H_2O^{18}]\ [CO^{16}O^{16}]/[H_2O^{16}][CO^{16}O^{18}] = 0.96$; for the system $D_2O - CO_2$ i.e. at high deuterium concentrations when the exchange is determined mainly by the reaction $D_2O^{18} + CO^{16}O^{16} \rightleftharpoons D_2O^{16} + CO^{16}O^{18}$, $\alpha_k = [D_2O^{18}][CO^{16}O^{16}]/[D_2O^{16}][CO^{16}O^{18}] = 0.98$ [9.10].

The value of $\Delta\rho_D/\rho_0$ in the original water is calculated from the measured values of $\Delta\rho/\rho_0$ and $\Delta\rho_k/\rho_0$.

The setup used for introducing the water into the reaction vessel and for subsequently pouring it out is shown schematically in Fig. 5. Before filling with test water, the filling setup and the vessels are rinsed. The sample is then introduced into the reaction vessel (about 50 or 120 ml depending on whether 10 or 25 ml pyknometers are used). The small amount of water remaining in the connecting tube outside the vessels is removed with filter paper. The connecting tube is sealed with a stopper. The vessel and sample are weighed and then filled with CO_2 gas* through a reducer, a capillary containing P_2O_5. About 300 g of CO_2 is introduced when about 50 ml of water is used, while about 600 g of CO_2 is introduced when about 120 g of water is used. The connecting tube is then sealed up again. Vessel plus water plus carbon dioxide are weighed. The isotopic exchange reaction is carried out in a water thermostat at 90°, the vessel being rotated (about half a revolution a minute). Repeated control experiments showed that at 90° the original carbon dioxide is found in isotopic equilibrium with natural water. ** Accordingly, the excess (or deficit) of the heavy isotopes of oxygen in the water, as compared with the normal isotopic composition, is distributed between the oxygen of the water and the oxygen of the CO_2, depening on the number of molecules of reactants and the partition coefficient between them. The weight of the vessel plus water and CO_2 was always the same before and after the reaction.

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*A standard 2 liter cylinder at an operating pressure of 150 atmospheres.

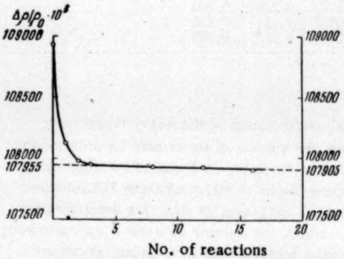

Fig. 6. Relation between the value of $\Delta\rho/\rho_0$ at 30° and the number of isotopic reactions; about 300 g of CO_2 and about 50 g of water were introduced into the vessel, C_D = 99.9%

It is also possible to determine the value of $\Delta\rho_D/\rho_0$ directly. Known amounts of test water and CO_2 are introduced into the reaction vessel as before. After isotopic equilibrium has been established the gas is released and a new lot of CO_2 introduced into the vessel and the reaction repeated a anew. Since the original carbon dioxide will be in isotopic equilibrium with the natural water, then as a result of several reactions, the isotopic composition of the oxygen in the water will approach the normal composition. By measuring the density of the water after all the reactions, we can find $\Delta\rho_D/\rho_0$ directly. The number of "reactions" required in an actual analysis can be readily determined on the basis of the number of gram molecules of water and CO_2 (in each reaction). From the curve in Fig. 6. it is obvious that initially $\Delta\rho/\rho_0$ drops sharply, and then (after three reactions) decreases very slowly and proportionally to the number of reactions. The linear portion of the curve is determined by the dilution of the sample with natural water. On an average, during each reaction $\Delta\rho/\rho_0$ decreases by about 0.0000025, and in three reactions decreases by about 0.0000075. But, after three reactions, excess of the heavy isotopes of oxygen remains in the sample, and determines the increase of 0.000006 in $\Delta\rho_D/\rho_k$. Moreover, as a result of several reactions, the test water is brought into isotopic equilibrium with the original carbon dioxide. Bearing in mind the distribution of O^{17} and O^{18} in nature, and also the differences in the partition coefficient α_k in the systems H_2O-CO_2 it is necessary to subtract a correction of 0.000004 from $\Delta\rho/\rho_0$. Thus, the over-all correction to be applied to the measured value of $\Delta\rho_D/\rho_0$ in the example just quoted is 0.000003 after three reactions.

As an example, curves for the establishment of isotopic equilibrium in the reaction vessel are shown in Fig. 7 for the systems H_2O-CO_2 and D_2O-CO_2.

Determination of the Concentration.

The concentration of deuterium in water is calculated from the relation [8]:

$$C_D = C_D^0 + A\frac{\Delta\rho_D}{\rho_D} + B\left(\frac{\Delta\rho_0}{\rho_0}\right)^2,$$

where $\Delta\rho_D/\rho_0$ is measured; C_D^0 = 0.00015 is the concentration of deuterium in natural water; A and B are coefficients determined by the masses of the stable isotopes of hydrogen and oxygen, their distribution in nature, and by the value at a given temperature t of the ratio of the densities $d_t^t = (\rho^{100}/\rho_0)$, where ρ^{100} is the density of 100% deuterium oxide with a normal isotopic composition for oxygen. The values of coefficients

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*We used liquid carbon dioxide produced from dry ice. Caron dioxide obtained as a byproduct in fermentation process cannot be used.

**The concentration of O^{17} and O^{18} is low in nature, while α_k approximates to unity and is only slightly dependent on temperature.

A and B and the values of d_t^t in the range 21-30° are given in Table 2. They are calculated on the basis of the values of d_{25}^{25} – 1.10772 [4] and the temperature relationship d_t^t [2].

Another, approximate method of calculation can be recommended for the determination of deuterium concentrations approximating to 100 %. Assuming that over a small range the concentration of deuterium is a linear function of $\Delta\rho_D/\rho_0$ we obtain $C_D = (\Delta\rho_D/\rho_0)/d_t^t - 1)$. Small concentrations of the heavy isotopes of oxygen (up to one percent) can be determined without taking into account the square member: $C_D = C_k^0 + A(\Delta\rho_k/\rho_0)$ where $C_k^0 = 0.00219$ [2.3].

TABLE 2

t° C	d_t^t	A	B	t° C	d_t^t	A	B
21	1,10742	9,2707	0,346	26	1,10779	9,2421	0,313
22	1,10750	9,2645	0,339	27	1,10786	9,2369	0,307
23	1,10758	9,2585	0,332	28	1 10792	9,2321	0,301
24	1,10765	9,2525	0,325	29	1,10798	9,2275	0,296
25	1,10772	9,2474	0,319	30	1,10804	9,2229	0,291

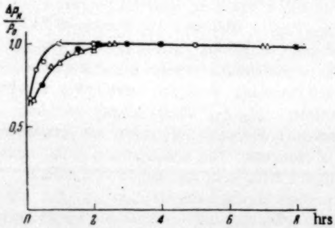

Fig. 7. Curves for the establishment of isotopic equilibrium (in relative units): O) about 300 g of CO_2 and about 50 g of water introduced into the vessel, C_D = 1% and G_k=1%; Δ) about 300 g CO_2 and about 50 g of water introduced into the vessel, C_D = 99.7%, C_k = = 1%.

When the concentration of the heavy isotopes of oxygen is known, the volume of water used for determining the concentration of deuterium is about 50 ml when using small pyknometers (about 10 ml), and about 120 ml when using large pyknometers (about 25 ml). For determination of both concentrations, the volume of water is approximately doubled. As a rule, samples with low concentrations are analyzed in 25 ml pyknometers, while samples with high concentrations are analyzed in 10 ml pyknometers. Irrevocable losses during analysis amount to less than 20% of the original volume of sample.

The authors wish to thank A. I Alikhanov and M. I. Kornfel'd for their interest in the work, and R. L. Serdyuk for valuable advice.

SUMMARY

A method for mass analysis has been developed which makes it possible to determine the deuterium concentration of water with an accuracy of ± 0.001% at very low concentrations, and with an accuracy of ±0.01% for very high concentrations (from about 99% and higher), as long as the concentration of the heavy isotopes of oxygen is known. Where it is necessary to measure the concentration of deuterium and that of the heavy isotopes of oxygen, the corresponding errors almost double.

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DETERMINATION OF SMALL AMOUNTS OF NITROGEN IN METALS AND ALLOYS

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Nitrogen is present in metals and alloys mainly in the form of nitrides. Determination of nitride nitrogen is usually carried out by distillation, this consists of getting the sample into solution, converting the nitrogen into ammonia, distilling the ammonia in a special apparatus, and titrating the solution obtained with acid, or the ammonia is determined photometrically.

Methods of dissolving metals and alloys are treated fairly adequately in the literature devoted to the determination of nitrogen [1-4]. For materials which are difficult to dissolve we can recommend a flask with a modified seal (Fig. 1), which prevents possible volatilization of the ammonia and too rapid evaporation of the acid used for dissolving the material. Many variants of the apparatus used for distilling the ammonia have been suggested [1-4].

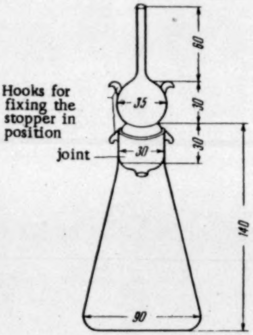

Fig. 1. Flask for decomposition of sample.

According to our experiments steam distillation is the most effective method. The somewhat modified construction of the basic part of the distillation apparatus is shown in Fig. 2. The various constructions which have been suggested for the splash head which prevents alkali from getting into the receiver, suffer from some drawback or other which is reflected in the results obtained, which can be either too high or too low. As experience has shown, the narrow tube of the splash head is usually filled with condensate, and the splashings of alkali which get into the splash head get mixed with the condensate in the tube, this liquid is then moved by the water vapor stream into the upper tubes of the apparatus, and, in this way the alkali can be partially trapped by the condensate in the receiver. The same thing happens when the condenser is placed directly over the distillation flask. In order to avoid this we suggest the use of a splash head with wide tubes (up to 10 mm) at the ends and with a widened part in the middle (Fig. 2). When the steam is sucked over slowly and uniformly, it partly condenses on the splash head walls, and washes the randomly falling splashes, and the liquid drops below without filling the tubes.

The correction in the blank experiment depends to a very large extent on the leaching out of the glass. Because of this, some parts of the apparatus (the splash head, condenser, and receiver) are made from quartz; this reduces the experimental error considerably.

For the determination of small amounts of nitrogen in metals and alloys a fairly sensitive photometric reaction is necessary. We have developed a photometric method for the determination of small amounts of nitrogen which is based on measuring the pH of the solution obtained during distillation (distillation of the ammonia), the pH is measured with the aid of a scale of matching filters and the appropriate universal indicator from the VIMS scheame used for determination of the pH of water [5]. By means of this method it is possible to determine thousandths and ten thousandths of a percent of nitrogen in the test material. By using dilute solutions or by decreasing the weight of sample, it is possible to determine up to tenths of a percent of nitrogen.

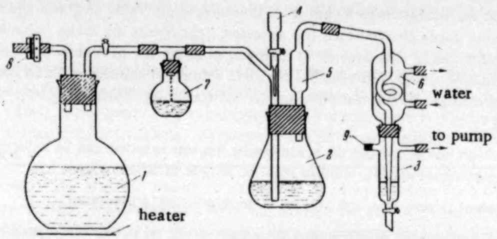

Fig. 2. Schematic diagram of the setup used for distillation of nitrogen
1) Steam generator (1-1.5 liter flask-; 2) distillation flask 300-400 ml; 3) quartz receiver; 4) funnel for introducing test solution; 5) quartz splash head; 6) quartz condenser (the long central part reaches right down into the receiver); 7) safety valve; 8) Hoffman clip for regulating the steam pressure; 9) opening for washing (under a rubber stopper).

The sensitivity of the method is 0.2 γ N in 1 ml. Photometric measurements after distillation of the ammonia does not take more than 2 minutes. The accuracy of the method is limited by the blank correction.

EXPERIMENTAL METHODS

0.1 to 3.0 g of metal or alloy is placed in the flask in which it is to be dissolved and the necessary amount of acid or mixture of acids — depending on the nature of the material to be decomposed — added. Dissolution is started in the cold, and then with heating; excess acid is best removed by evaporation. The transparent residue in the flask is diluted to 100-150 ml with distilled water.

Towards the end of the dissolution process the apparatus is prepared ready for distillation of the ammonia. The water is brought to the boil in the steam generator and steam passed through all the apparatus for 10-15 minutes, the condensate which collects in the receiver and the distillation flask being then rejected. 50 ml of NaOH (500 g/liter) is introduced into the distillation flask and steam passed through with slow suction (about 100 bubbles a minute) for 10-15 minutes, after which the vacuum is switched off, the tap of the separating funnel over the distillation flask is opened and the steam switched off. The liquid is poured out of the receiver and rejected. 5 ml of the working solution of H_2SO_4 is accurately measured into the receiver through the side tube and the latter then closed with a stopper. The test solution is then slowly poured through the funnel into the distillation flask, the flask being swirled continuously all the time. The walls of the flask and funnel are washed with the smallest possible lots of water and the tap of the funnel closed. The tap through which steam is passed into the distillation flask is opened, and the liquid in the latter agitated for some time, the vacuum is then switched on. As soon as the liquid in the distillation flask has been heated up to the boiling point, the steam passes into the splash head and the tubes leading into the condenser and heats them. From this point the distillation is carried out for 15 minutes with regular boiling and under weak suction. The ammonia liberated is taken over by the steam and dissolves in the condensate formed, and is collected in the receiver. Usually 30-40 ml of liquid are collected by the end of distillation. The vacuum is switched off and the tap of the funnel rapidly opened so as to let air into the distillation flask, the steam is then switched off. The splash head and condenser are disconnected and the distillate obtained poured into a 50 ml standard flask. The condenser and receiver are washed with twice distilled water dispensed from a special wash bottle, and the washings collected in the same standard flask. The solution in the standard flask is made up to the mark with water and the whole thoroughly mixed. Photometric measurements are then made.

For this purpose a drawing board with a scale of matching light filters is placed on a white sheet of paper while a plate with empty cells is placed on the left hand side. Into one of these empty cells is measured out exactly two drops of universal indicator, while with another pipet, test solution is withdrawn from the flask and 5 drops of it placed in the same cell. The plate is slightly shaken by tapping with the finger so that the test solution is mixed with the indicator. The color of the test solution is then compared immediately with the scale of matching colors, and the nearest match chosen. The required pH value is given against the corresponding light filter. When the color shade lies between two adjacent light filters the mean value is taken. On the basis of a table compiled beforehand, the amount of nitrogen to which the pH value found corresponds is then established (the table is compiled taking into account the total volume of solution). From the amount of nitrogen thus found the percentrate of nitrogen in the test material is then found (by multiplying by 100 and dividing by the weight of sample taken).

When the pH value is high and is outside the scale limits the test solution can bc diluted appropriately with null solution. For more accurate results, another smaller sample is taken.

When the nitrogen content is very low, the aliquot is correspondingly increased.

Determination of small amounts of nitrogen should be carried out on two or three parallel aliquots, one or two blank runs being carried out as well through all the stages of the analysis, the conditions being kept strictly constant.

It is obvious of course that the reagents used for the analysis should be as pure as possible so as to cut down the blank correction.

Photometric measurements should not take more than 1-2 minutes, since on standing, the color of the test solution may change leading to higher or lower pH values as the result of the action of the air.

Experimental Conditions

No work involving nitric acid, ammonia, or ammonium salts should be carried out in the room where nitrogen determinations are carried out. The air should be neutral (no acid or alkaline vapors should be present in the air).

Vessels (flasks, beakers, wash bottles, pipets, etc) and also the apparatus used for distilling the ammonia should, before starting the analysis, be washed out carefully and steamed, and should only be used for this particular work in future.

The same wash bottle should not be used for transferring the acid solution into the distillation flask, and for washing the parts of the condenser and receiver after distilling the ammonia, since in the first instance there is a danger of sucking up acid vapors into the wash bottle which will affect the pH of the water in this bottle. The edges of the vessels should not be touched with the tip of the wash bottle during washing. The wash bottle should be operated with a rubber bulb so as not to affect the pH of the water.

The stock and working solutions of ammonia and acid, as well as the indicators (see reagents) should be prepared immediately before an analysis, and only in sufficient amount for the work in hand. Compilation of the table, carrying out the series of blank experiments, and determination of nitrogen in the samples, should all be carried out with the same solutions. When any reagent or indicator has to be prepared anew, it is necessary to check before everything, the table, starting with the null solution, so as to establish whether there has been any shift of the color shade with respect to the quoted values. If they are stored for some time, the indicator and solutions should be checked from time to time against the scale.

The indicator and board with the scale of matching light filters must not be left exposed to light. After comparison the board should be stowed in a container.

The pipets used for the indicator and test solution are best made from similar tubes and should have openings of the same diameter at the tip. The size of the drops should be constant; for this purpose the pipet should be held strictly perpendicular during drainage. The pipets used for compiling the table should also be used for the determination of nitrogen in samples. If the pipets are changed then the table should be checked.

It has been observed that during the transfer of very strongly acid test solutions into the distillation flask without taking any special precautions, acid vapors appear in the flask above the liquid, these vapors on being sucked into the receiver distort the results considerably. Accordingly, acid test solutions should, if possible, be diluted, and during their transfer into the distillation flask should be introduced carefully through a funnel with a narrow internal tube (Fig. 2) the distillation flask being given a constant swirling motion during the addition.

When working with boards of VIMS matching light filters we used intervals which define the color changes more clearly. Thus, boards with pH values from 4 to 8 are only suitable for work in the range 4.5 to 7.2.

Reagents

Twice-distilled water is prepared in an all-glass distillation apparatus. The distillate is poured into a 3-4 liter distillation flask to fill the latter to two-thirds of its volume, it is then acidified with sulfuric acid and colored violet with MnO_4. Not more than two-thirds of the volume taken is distilled. The pH is measured by means of the scale of matching light filters. By maintaining standard conditions water whose pH is always the same can be obtained.

Sodium Hydroxide (500 g/liter), free from ammonia. Test for freedom from ammonia by taking 50 ml of the sodium hydroxide solution in a distillation flask and dilute with 100 ml of water free from ammonia; steam distillation is then carried out as usual for 15 minutes. Any ammonia is determined by the method indicated above by measuring the pH.

Hydrochloric or Sulfuric Acid (1:1) or other acids required for decomposing the samples should be free from ammonia. Their ammonia content is checked by diluting 25 ml of acid with 100 ml of water free from ammonia, and transferring the solution carefully through a funnel into a distillation flask containing 50 ml of sodium hydroxide which has previously been checked for its ammonia content. Distillation is carried out as usual and the ammonia content determined on the basis of the pH value.

Determination of Nitrogen in Standard Samples

Samples	Specified content of N, %	N actually found, %	Sample weight, g
Steel No.207	0,006	0,004	5
		0,004	1
		0,004	2
		0,004	3
Steel No.206	0,013	0,014	0,5
		0,011	0,5
		0,012	0,5
		0,013	0,5
Steel No.159	0,11	0,107	0,1
		0,103	0,1
		0,112	0,2

Standard 0.05 N ammonia solution is prepared by diluting a concentrated solution. 3.4 ml of 14.97% NH_4OH is diluted with twice distilled water to 1 liter. The solution obtained contains approximately 0.0007 g of N per ml. The solution obtained contains approximately 0.0007 g of N per ml. The solution is standardized against 0.05 N H_2SO_4.

The working solution of 0.001 N NH_4OH which is used for compiling the Table is prepared by diluting the standard solution. 1 ml of the 0.001 N working solution contains 0.000014 g N.

H_2SO_4 Solution. A stock solution of 0.05 N H_2SO_4 is prepared first. The working solution – used for the scale with a value of 4 to 8 – is prepared by dilution. 30 ml of 0.05 N H_2SO_4 is diluted with twice distilled water to 1 liter. 5 ml of this solution on dilution to 50 ml should have a pH of about 4.5-4.7. This solution is the null solution for compiling the Table (see below). In view of the instability of the working solution it should be periodically checked.

Universal Indicator for the scale of matching light filters with pH values from 4 to 8. First solution; 0.1 of bromothymol blue is dissolved in 50 ml of ethanol, and 150 ml of twice distilled water heated to 80° added, the whole is mixed and 3 ml of 0.05 N NaOH added. Second solution: 0.05 g of methyl red is dissolved in 50 ml of ethanol and 20 ml of twice-distilled water heated to 90° added, 3.75 ml of 0.05 N NaOH is added to the hot solution. On cooling, the two solutions are mixed in the proportion of 1:1.

Table for Determination of Nitrogen on the Basis of the pH Value.

The Table is compiled by distilling various amounts of the standard ammonia solution in the range 14 to 200 γ. The null solution serves as the origin for the Table. 5 ml of the working solution of H_2SO_4 accurately measured out is always placed in the receiver and the distillation carried out for 15 minutes, the pH is measured as indicated for the analytical procedure. The table is operative over the pH range 4.5 to 7.2 (the extreme pH values on the scale of matching light filters are poorly distinguishable with respect to their colors).

On switching over to a scale with pH values ranging from 0.1 to 4.0 or from 8 to 11.8, respectively, the universal indicator is changed and another working solution of H_2SO_4 with an appropriate concentration is used, while another Table for determination of nitrogen on the basis of the pH value is compiled. The scale of matching light filters is shown in Fig. 3.

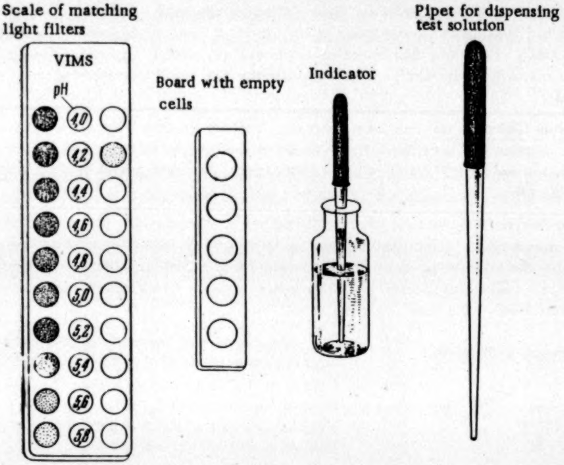
Scale of matching light filters
VIMS
pH
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
Board with empty cells
Indicator
Pipet for dispensing test solution

Fig. 3. Apparatus for pH determination.

SUMMARY

A new method has been developed for the determination of small amounts of nitrogen, it is based on measuring the pH of the solution obtained as a result of distillation apparatus is suggested, and a detailed description of the method is given.

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ULTRAMICROCHEMICAL STUDY OF THE COMPOSITION OF THE CELL SAP OF PLANKTON DIATOMS

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In connection with solving the problem of the buoyancy of plankton diatoms [1] the necessity arose of carrying out a chemical analysis of the cell sap of these alga. But, since the volume of the sap of even the largest of them, the so called giant tropical diatoms Ethmodiscus rex (Centrales) is only 0.5-1.5 mm^3, studies of this sap could only be carried out by means of the ultramicro method of chemical analysis [2]. Samples of the diatom Ethmodiscus were collected by K. V. Beklemishev and G. I. Semina during the voyage of the "Bityazya" in the Spring of 1955. The sap which was extracted from them by means of a piston ultramicro pipet was transferred to quartz micro vessesl with a diameter of 0.5-1.5 mm fused into glass capillaries containing a small amount of distilled water for lowering the rate of evaporation of the sap; the initial length of the column of liquid was measured under the microscope. The samples were given to us in this form for investigation.

The capillary was opened and the micro vessel removed and placed in a moist chamber on the object stage of a microscope. Twice-distilled water was added so as to bring the length of the column of liquid in the vessel to its original value, it was then centrifuged in order to mix the contents, and the volume of sap measured in a standard capillary. The sap was then returned again to the vessel and aliquots taken for determination of Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, and sO_3^{2-}. For this purpose, four moist chambers were used: one for determination of Na^+ and Mg^{2+}, another for Ca^{2+} and K^+, a third for SO_4^{2-}, and a fourth for Cl^-.

The chemical methods were chosen bearing in mind the characteristics and possibilities of ultramicro analysis. We endeavoured also to choose methods which would enable the minimum volume of sap to be used for each determination, and would make it possible to carry out parallel determinations for each of the ions in most cases.

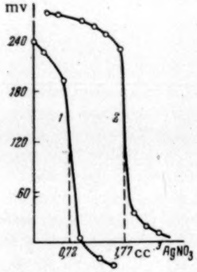
The techniques chosen were tried out beforehand on solutions (imitating sea water) taken in identical volumes, and obtained results which were in satisfactory agreement with calculated results. The Table contains results for the analysis of sea water. Descriptions are given below of the chemical techniques used for determination of each of the ions in cell sap.

Analysis of Sea Water.

Taken, μg	Found, μg	Error, %	Taken, μg	Found, μg	Error, %	Taken, μg	Found, μg	Error %
Cl^-			Na^+			K^+		
0,330	0,327	−1	0,23	0,236	+3	0,033	0,031	−6
0,412	0,42	+2	0,24	0,244	+2	0,033	0,036	+10
Ca^{2+}			Mg^{2+}			SO_4^{2-}		
0,0348	0,0365	+5	0,0055	0,0058	+7	0,23	0,24	+5
0,033	0,0310	−7	0,0055	0,0050	−10	0,23	0,245	+8

Determination of Chloride

For determination of chloride, in contrast ot the Mohr or Volhard methods [3] which are generally adopted for analysis of sea water, we,adopted the method of potentiometric titration [4] using 0.01 N silver nitrate for titration, the latter having also been standardized potentiometrically against 0.01 N NaCl. 0.020-0.025 mm^3 was measured in a standard capillary for each determination and transferred into the titration vessel filled before hand with 1 mm^3 of 0.02 N H_2SO_4; in this way an approximately 0.01 N solution of the chloride to be titrated was obtained. The titrant was added in aliquots of about 0.2 mm^3. In all cases well defined titration curves were obtained which were in good agreement with each other in parallel determinations. Titration curves for two samples are given as an example (diagram). The technique used for potentiometric ultramicrotitration has been described previously [5].



Potentiometric determination of chloride in cell sap.

Determination of Sodium

0.025-0.030 mm^3 of sap was measured in a standard capillary and transferred into a vessel with a diameter of 2mm containing about 1 mm^3 of twice-distilled water, 5 mm^3 of a saturated solution of zinc uranyl acetate was added and the mixture allowed to stand for 3 hours. 24 hours, which is the usually recommended time of standing, proved to be unnecessarily long in the case of ultra micro determination, and was also inconvenient since it is very difficult to keep such a small volume of solution constant in the course of such a long time, and appreciable increases or decreases in the volume lead to experimental error.

The precipitate of $NaZn(UO_2)_3\ (CH_3COO)_9 \cdot 6H_2O$ which separated out was separate by centrifuging, and was washed successively with acetic acid, and ether [6] and finally dissolved in 1.5- 2mm^3 of water, 2-3 crystals of solid $(NH_4)_2CO_3$, 0.2-0.3 mm in diameter being added by means of the sealed tip of a pipet during this process, 0.1- 0.2 mm^3 of 3 N NH_4OH was finally added. The solution was titrated with 0.1 M Complexon III solution using eriochrome black T as indicator [7] on a white background; the color change was observed with the naked eye. Here as for all titrimetric determinations, a buret with an adjusting micrometer was used [5].

Determination of Calcium

0.1 mm^3 of sap, as for the case of Na^+, was transferred to a vessel containing 1 mm^3 of twice distilled water, 0.3 mm^3 of 1 N NaOH was added and the solution titrated with 0.01 M Complexon III using murexide [7] as indicator on a white background; titration was carried out against an untitrated reference standard so as to establish the color change more accurately. Ca^{2+} was also determined in sea water and in several sap samples amperometrically, excess Ce^{4+} being titrated with Mohr's salt at E = +1 volt, after dissolving the precipitate of calcium oxalate. The results obtained when this technique was used were in good agreement with the complexonometric results. The amperometric titration technique has been described previously [8].

Determination of Magnesium

Mg^{2+} ions, in contrast to the hydroxyquinoline method [3] usually adopted for analysis of sea water, was determined by means of the reaction with titan yellow since a small content of this metal was expected. 0.005-0.1 mm^3 of the sap was transferred to a vessel containing 0.3 mm^3 of distilled water, and 0.1 mm^3 each of 5% saccharose solution and hydroxylamine hydrochloride added, followed by 0.05% titan yellow solution and 0.5 mm^3 of 1 N NaOH solution. The solution obtained was transferred to a coloriscopic capillary 0.3 mm in diameter and 10 mm long, and the color compared with a standard solution prepared in the same way.

Determination of Sulfate Ions

Sulfate ions were determined photometrically with barium chloranilate [9]. In order to remove ions which interfere with determination of the sulfate ions, a capillary column 1 mm in diameter and 5-7 mm long packed with the ion exchange resin KU-2 was used. Into this column, without touching the resin level, about 0.3 mm^3 of twice distilled water and 0.1 mm^3 of sap were introduced. This column was then placed in another capillary tube of the same diameter, one end of which was sealed, the column with the ion exchange resin was fitted into the second capillary so that the end of the former did not touch the bottom of the latter; centrifugation was then used to drive the liquid through the resin. The second capillary was also used for collecting 0.3 mm^3 of wash water passed through the resin. Having fixed the capillary in a holder, about 0.1 mm^3 of 2% NH_4OH solution was added to the acid solution obtained, this was followed by 0.2 mm^3 0.05 M potassium hydrogen phthalate, about 1 mm^3 of ethanol and some solid barium chloranilate, the latter being added "on the tip of a pipet" (see above(. The precipitate of sulfate and excess barium chloranilate was removed by centrifugation. The colored solution was compared with a standard solution prepared in the same way, comparison being made in coloriscopic capillaries.

Determination of Potassium

When an element forms a compound which separate out in the form of a comparatively bulky, fine crystalline precipitate, the element can be determined ultramicrochemically on the basis of the volume of this precipitate with an accuracy of ±10% [10]. Essentially, the method consists of preparing, and collecting by centrifuging, precipitates from test and standard solutions under identical conditions, the precipitates being collected in the top of the corresponding vessels. The height and diameter of the base of the precipitates, which are conical in form, are measured on the micrometric scale of a microscope and their volumes calculated. Knowing the content of the test element in the precipitate obtained from the standard, its content in the precipitate obtained from the test solution can be calculated. We used this method for determining potassium as $K_2NaCo(NO_2)_6$ [11]. To 0.1 mm^3 of sap was added 0.05 mm^3 of reagent, the solution was allowed to stand for 30 minutes and then centrifuged at the same time as a precipitate obtained in the same way from a standard solution; the precipitates were carefully collected in the top of the vessels.

SUMMARY

An ultramicro method has been developed for the determination of six elements in a volume of about 0.5 mm^3. Results were obtained for a standard solution which were in satisfactory agreement with calculated data. The composition of the cell sap of Ethmodiscus diatom has been studied.

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THE SEPARATE DETERMINATION OF PEROXIDE AND SUPERPEROXIDE OXYGEN IN SUPERPEROXIDES

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Until recently, for defining the concept of "inorganic peroxide compounds", it was considered adequate to indicate the presence in their molecules of a pair of oxygen atoms, the so called "oxygen bridge." In order to establish the composition of these compounds the "active oxygen" which is liberated during the break down of the "oxygen bridge" is usually determined by a permanganometric, iodometric, or gasometric method. A. more detailed study of the structure and composition of a number of representatives of this large class of compounds has shown that some of them differ essentially with respect to the nature of the bonds between the oxygen atoms in the "bridge." In particular, it has been established that the crystal lattices of the peroxides consist of metal ions and of molecular anions of O_2^-, with the structure $[\,:\overset{..}{\underset{..}{O}}:\overset{..}{\underset{..}{O}}:\,]^{-2}$ [1, 2], while the crystal lattices of the superperoxides consists of metal ions and of molecular anions of O_2^-, with the structure $[\,:\overset{.}{\underset{..}{O}}-\overset{..}{\underset{.}{O}}:\,]$ [2, 3]. The difference in the nature of the bond between the oxygen atoms in the bridge of the peroxide and superperoxide shows up particularly clearly during hydrolysis. Peroxides hydrolyze according to the equation $Me_2O_2 + 2H_2O = 2MeOH + H_2O_2$ with formation of hydrogen peroxide which can be quantitatively titrated permanganometrically in an acid medium. Superperoxides hydrolyze according to the equation: $2\ MeO_2 + 2H_2O = 2\ MeOH + H_2O_2 + O_2$. Consequently, in superperoxides, 2/3 of the "active" oxygen which we shall call "superperoxide oxygen" is liberated in the form of O_2, while 1/3 which we shall call "peroxide oxygen" is liberated as H_2O_2. Separate determination of peroxide and superperoxide oxygen on one aliquot by decomposition of the superperoxides with water cannot be realized. The alkali thereby formed leads to decomposition of the H_2O_2 and to distortion of the analytical results. Seyb and Kleinberg [4] have developed a gasometric method for the determination of peroxide and superperoxide in NaO_2 and KO_2, their method consists of adding 5 ml of a buffer mixture-diethyl-phthalate – to about 0.2 g of sample, this is followed by 10 ml of a mixture of glacial acetic acid (8 ml) and diethyl-phthalate (2 ml). When this is done only superperoxide oxygen is liberated. In order to determine the peroxide oxygen formed in the acetic acid solution, the hydrogen peroxide is decomposed by addition of 15 ml of a mixture of 1 M HCl and 3 M $FeCl_3$, n and the volume of oxygen thereby liberated measured.

We have established that the method of Seyb and Kleinberg gives reproducible results during the analysis of the superperoxides o the alkali metals. Nevertheless, it must be emphasized that this method is only suitable when the superperoxide oxygen content of the test samples is appreciable. It is not applicable for the analysis of preparations containing superperoxides as impurities, in view of the necessity of using samples considerably greater than 0.2 g, and consequently, large valumes of reagents and large gas burets. In order to determine superperoxide and peroxide oxygen in preparations containing the superperoxides of the alkaline-earth metals as impurities, we used the technique described in [5]where dilute CH_3COOH is used instead of diethyl phthalate. Nevertheless, it was subsequently observed that peroxide oxygen can be determined by titrating with 0.1 N $KMnO_4$, the peroxide oxygen that is formed in acetic acid solution during the gasometric determination of superperoxide by the Seyb method, since the presence of diethyl phthalate in the solution being titrated does not essentially affect the results of the determination. At present, determination of superperoxide and peroxide oxygen on one aliquot (about 0.3 g) is carried out as follows. Superperoxide oxygen is determined gasometrically by Seyb's method. During this process a gas is liberated on treating an aliquot with acetic acid, analysis is also carried out for CO_2, since the presence of carbonate as an impurity in superperoxides is unavoidable. Peroxide oxygen is determined permanganometrically by titrating an aliquot part of the acetic acid solution containing diethyl phthalate, after making the volume of the solution up to 250 ml and acidifying with H_3PO_4 (1 : 4). In the Table are given results for the determination of peroxide and superperoxide oxygen in samples of technical NaO_2, KO_2, and in peroxide preparations of calcium, strontium, and barium containing $Ca(O_2)_2$, $Sr(O_2)_2$ and $Ba(O_2)_2$ as impurities, the latter being prepared according to a method described in [6-8]. The reliability of the determination of peroxide oxygen was confirmed by a control analysis carried out on a separate aliquot.

Determination of Peroxide and Superperoxide Oxygen in Superperoxides

Test material	Peroxide oxygen on a separate aliquot, % wt.	Sample weight	Peroxide oxygen on a separate aliquot, % wt	ml/g of superperoxide oxygen *	Superperoxide oxygen, % wt	Me^IO_2, % wt.
Technical NaO_2	12.40	0,3040	12,38	184,53	26,37	90,75
Technical KO_2	10,91	0,3020	10,91	150,89	21,56	95,60
Peroxide preparation of:						$Me^{II}(O_2)_2$ Wt.%
Ca	13,87	0,3207	13,83	38,91	5,56	18,08
Sr	8,78	0,3011	8,75	18,79	2,68	12,74
Ba	7,87	0,2941	7,84	9,01	1,28	8,09

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*At normal temperature and pressure.

It is clear from the table that the deviation observed during the determination of peroxide oxygen on a separate aliquot without treatment with diethyl phthalate and CH_3COOH, and on an aliquot of the acetic acid solution containing diethyl phthalate, is of the order of 0.03%.

By converting into peroxide and superperoxide, and taking into account the results of the determination of CO_2 by the Fresenius method, and the amount of free alkali, the composition of the preparations indicated can be expressed in % wt. by the following figures:

1) 90,75 Na_2O_2, 3,84, Na_2O_2, 0,70 Na_2CO_3, 4,71 NaOH (by difference)
2) 95,60 KO_2, 2,36 K_2O_2, 1,66 K_2CO_3, 0,38 KOH (by difference)
3) 18,08 $Ca(O_2)_2$, 49,96 CaO_2, 10,29 $CaCO_3$, 21,67 $Ca(OH)_2$.
4) 12.74 $Sr(O_2)_2$, 55,70 Sr_2O_2, 15,82 $SrCO_3$, 16,74 $Sr(OH)_2$.
5) 8,09 $Ba(O_2)_2$, 76,46 BaO_2, 14,11 $BaCO_3$, 1,44 $Ba(OH)_2$.

SUMMARY

It has been shown that during the analysis of preparations containing peroxide and superperoside, gasometric determination of peroxide oxygen can be successfully replaced by titrating with 0.1 N $KMnO_4$ an aliquot part of the acetic acid solution containing diethyl phthalate, formed during the gasometric determination of superperoxide oxygen.

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THE OXIDATION OF DIALKYL- AND DIARYLDITHIOPHOSPHATES BY IODINE AND THEIR TITRIMETRIC DETERMINATION

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In neutral and acid media the reaction between dialkyl- and diaryldithiophophotic acids and iodine proceeds according to the equation

$$2(RO)_2PSS^- + I_2 = (RO)_2PSS-SSP(OR)_2 + 2I^-.$$

The reaction is slightly reversible [1-2], accordingly, direct titration with iodine of solutions of the dithiophosphates must be carried out to the appearance of an intense blue color of the starch (not lilac). Satisfactory results are obtained during titration of excess iodine with thiosulfate, or during the titration of non-colored dithiophosphates in the presence of organic solvents heavier than water (CCl_4, $CHCl_3$).

Our studies have shown that readily reproducible, and very accurate results, are obtained by the oxidation of dithiophosphates with excess iodine (more accurately hypoiodide) in an alkaline medium.

For establishing the equation of the reaction between iodine and nickel diethyldithiophosphate, to a known volume of a standard solution of the latter is added 6 N NaOH and excess of a standard iodine solution. After addition of iodine the concentration of the alkali should be about 1 N. The mixture is allowed to stand for 5-10 minutes, after which it is neutralized with acid and excess iodine is titrated with thiosulfate. Completion of the oxidation of dithiophosphate by iodine can be established on the basis of the clarification of the solution with the disappearance of the disulfide originally formed.

TABLE 1

Oxidation of Nickel Diethyldithiophosphate in an Alakaline Medium

$[(C_2H_5O)_2PSS]_2Ni$ taken, mg	Amt. of I_2 used for oxidation (N_{I_2} = 0,08878), ml	$\frac{M_{I_2}}{M_{[(C_2H_5O)_2PSS]_2Ni}}$
6,7	5,6	15,87
6,7	5,7	16,15
6,7	5,7	16,15
41,3	34,8	16,03
38,5	32,45	16,02
21,9	18,44	16,02
13,4	11,3	16,02
26,8	22,7	16,01
26,8	22,7	16,01

When solid dithiophosphate is taken, care must be taken before addition of iodine to decompose the phosphate completely with alkali, since parts of it may be insulated from the action of the oxidizing agent by the metal hydroxide which is formed. In order to ensure complete breakdown of the dithiophosphates of nickel, bismuth, and some other elements, it is necessary to moisten them with a drop of CCl_4 or some other solvent, and then added the necessary amount of alkali and shake the mixture so as to transfer the dithiophosphate into the aqueous phase. The procedure outlined above is then followed.

It follows from Table 1 that 16 moles of iodine correspond to one mole of nickel diethyldithiophosphate. Similar results are obtained with pyridine diphenyldithiophosphate. After oxidation of the dithiophosphate with iodine, sulfate ions can be detected in solution. Phosphate ions are absent. This leads one to conclude that in a strongly alkaline medium iodine oxidizes dithiophosphates to sulfate. The reaction can be depicted by the equation $(RO)_2PSS^- + 16I_2 + 40OH^- = (RO)_2POO^- + 4SO_4^{2-} + 32I^- + 20H_2O$, where R is an alkyl or aryl radical.

TABLE 2

Determination of Metal Dithiophosphates in an Alkaline Medium

	Dithiophosphate, mg		Error			Dithiophosphate, mg		Error	
	Taken	Found	In mg	In %		Taken	Found	In mg	In %
$[(CH_3O)_2PSS]_2Ni$	44,3	44,3	0	0	$[(C_2H_5O)_2PSS]_2Pb$	16,85	16,95	+0,1	+0,6
$[(C_2H_5O)_2PSS]_2Ni$	41,3	41,35	+0,05	+0,1	.	48,4	48,0	—0,4	—0,8
.	38,5	38,6	+0,01	+0,3	$[(C_2H_5O)_2PSS]_3Bi$	68,2	68,3	+0,1	+0,1
.	21,9	21,9	0	0	.	13,59	13,39	—0,2	—1,5
$[(C_2H_5O)_2PSS]_2Cd$	45,6	45,6	0	0	$[(C_2H_5O)_2PSS]_3In$	71,9	72,0	+0,1	+0,1
.	69,9	70,3	+0,4	+0,6					

Oxidation of nickel diethyldithiophosphate proceeds rapidly in a strongly alkaline medium. Changes in the alkali concentration over the range 0.5-1.5 N only affects the rate of oxidation, and does not affect the amount of iodine used up. When the alkali concentration of the solution is 1 N, the time required for complete oxidation of nickel diethyldithiophosphate is 5-10 minutes. The amount of iodine used up is independent of the excess of it used. The order in which the alkali and iodine is added affects the amount of iodine used up only when excess of the latter is immediately titrated with thiosulfate (after acidification). When the solution is kept for 10 minutes prior to titration, the order in which alkali and iodine is added has no effect on the amount of iodine used.

The oxidation reaction of dithiophosphates in an alkaline medium permits determination of small amounts of these compounds with a high degree of accuracy. The method is particularly suitable in those cases when the dithiophosphate has a low melting point which excludes the possibility of drying it at 105° (the dithiophosphates of lead, bismuth, etc). The results obtained (Table 2) testify to the high accuracy of the determination.

TABLE 3
Titrimetric Determination of Cadmium

Cadmium, mg		Error	
taken	found	in mg	in %
11.24	11.21	− 0.03	− 0.3
5.62	5.65	+ 0.08	+ 0.5
0.562	0.550	− 0.012	− 2
0.562	0.562	0	0

Results for the determination of cadmium are given in Table 3. The cadmium is precipitated in a neutral or acid medium with a 1.5-2 fold excess of 0.05 N nickel diethyldithiophosphate, the precipitate and solution are allowed to stand for 5-10 minutes, after which an equal volume of water is added, if the cadmium concentration of the test solution is greater than 0.01 M. the precipitate is filtered through a No. 3 glass crucible, and washed 3-4 times with water. The precipitate is treated with alkali and excess iodine added (after addition of iodine the concentration of the alkali should be 1 N), during this stage the solution initially becomes turbid as a result of the formation of the disulfide, the solution subsequently clarifies. The clear solution is neutralized with sulfuric acid and the excess iodine titrated with thiosulfate.

Our experiments showed that ethylenediaminetetracetic acid is not oxidized by iodine in a medium of 2 N NaOH even on standing for a long time (12 hours). Nevertheless, ethylenediaminetetracetic acid is not suitable for keeping metals in solution during treatment of metal dialkyl- and diaryldithiophosphates with iodine in the presence of 2 N NaOH, since at such high alkali concentrations, the complexonates of most metals (Cd, Cu, Bi, Ni) are decomposed completely or partially with the formation of hydroxides. Only those metals which form amphoteric hydroxides (Pb, Cr) remain in solution.

SUMMARY

The oxidation of dithiophosphates by iodine in a strongly alkaline medium proceeds according to the equation:

$$(RO)_2PSS^- + 16I_2 + 40\,OH^- = (RO)_2\,POO^- + 4\,SO_4^{2-} + 32I^- + 20\,H_2O$$

and is a suitable basis for the accurate titrimetric determination of small amounts of elements in the form of their dithiophosphates.

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NEW SENSITIVE REACTIONS FOR THE DETECTION OF COPPER IONS

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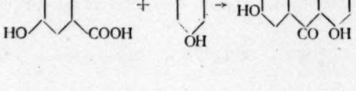
Copper ions strongly accelerate the atmospheric oxidation of an ammoniacal solution of o-aminophenol. An ammoniacal solution of o-aminophenol is colored a yellow-green color as a result of the action of air; copper ions strongly accelerate this reaction.

Detection of copper ions on the basis of the catalytic acceleration of the atmospheric oxidation of an ammoniacal solution of o-aminophenol is carried out as follows. To 1 ml of test solution is added 0.2 ml of a 1% solution of ammonia and 0.1 ml of a 0.01% aqueous solution of o-aminophenol, and the mxiture shaken. The color of the test solution and that of a control solution is observed after 1-2 minutes. When copper ions are present in the test solution, the yellow-green color appears more rapidly and is more intense than in the case of the control solution. It is possible to detect as little as 0.01 γ of Cu in 1 ml of solution at a limiting dilution of 1:100,000,000. When 0.2-0.1 γ of Cu is present in 1 ml of solution, i.e. at a limiting dilution of 1:5,000,000 - 1:100,000,000, the yellow-green color of the test solution appears during the course of one minute while in the control solution it only appears after 1 minute. At even greater dilutions the color in the test solution appears after 2-3 minutes, while in the case of the control solution the color only appears after 6-8 minutes. Silver ions also accelerate the atmospheric oxidation of an ammoniacal solution of o-aminophenol but to a lesser extent than copper. 1 γ of Ag in 1 ml of solution at a limiting dilution of 1:1,000,000 can be detected by means of its accelerating effect on the atmospheric oxidation of an ammoniacal solution of o-aminophenol.

Cation	Limit of identification, λ/ml	Limiting concentration
Cu^{2+}	0.1	1:10,000,000
Fe^{3+}	0.1	1:10,000,000
Al^{3+}	0.1	1:10,000,000
UO_2^{2+}	2.0	1:500,000
Th^{4+}	5.0	1:200,000
Ni^{2+}	20.0	1:500,000

The alkali and alkaline-earth metals as well as Mg, Be, Al, Zn, Cd, Se, Te, Fe^{3+}, Ni, Co, Pb, Mn^{2+}, Th^{4+}, Zr^{4+}. UO_2^{2+}, Ce^{3+}, Ti^{IV}, VO_3^-, MoO_4^{2-}, WO_4^{2-}, AsO_3^{3-}, PO_4^{3-}, do not interfere with the detection of copper. Copper can be detected in the presence of elements which are precipitated by ammonia (Mn, Be, Mg, etc.) at a ratio of these elements to copper of 2000:1. In the latter instance when copper is present, the change in color occurs appreciably more rapidly in the clear layer above the precipitate than in a color test.

We have also studied the reactivity of copper ions with an alcoholic solution of euxanthone $C_{13}H_8O_4$. Euxanthone is the product obtained by the condensation of hydroquinone carboxylic acid and resorcinol on boiling with acetic anhydride:



An alcoholic solution of euxanthone forms with copper salts a yellow color the intensity of which increases with increasing copper concentration. To 1 ml of an almost neutral test solution (at a pH of 6-6-7.4) is added 0.2 ml of a 0.02% alcoholic solution of euxanthone and the whole shaken. A control test is carried out simultaneously, i.e. the reagents indicated are added in the same amounts to 1 ml of distilled water and the whole shaken; after 1-2 minutes the colors of the test and control solution are compared. When copper is present in the test solution a yellow color appears; the control solution remains colorless. 0.1 γ of Cu can be detected in 1 ml of solution by means of euxanthone.

Trivalent iron, aluminum, divalent nickel, thorium, and uranium (Table also react with euxanthone to give a yellow color.

Euxanthone permits detection of 1γ of Cu in 1 ml of solution in the presence of 1000 times its amount of Li, K, Na, Ag, NH_4^+, Rb, Mg, Sr, Ca, Zn, AsO_4^{3-}, in the presence of 100 times its amount of Pb, Ce, Te, and Ti, in the presence of 10 times its amount of Ba, and in the presence of 5 times its amount of MoO_4^{2-}

SUMMARY

A new selective catalytic reaction is described for the detection of copper ions; it is based on acceleration of the atmospheric oxidation of an ammoniacal solution of o-aminophenol, there being an appreciably more rapid change in the color of the solution when copper is present. Silver interferes.

Euxanthone $C_{13}H_8O_4$ can be used for the detection of Cu^{2+}, Al, Fe^{3+}, UO_2^{2+}, Th^{4+}, and Ni^{2+}. An alcoholic solution of the reagent reacts with the ions listed at a pH of 6.6-7.4 to give a yellow colored solution.

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SPECTROGRAPHIC DETERMINATION OF SMALL AMOUNTS OF HAFNIUM DIOXIDE IN ZIRCONIUM DIOXIDE

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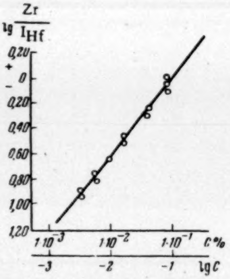
Spectrographic methods allow the determination of hundredths and tenths of a percent hafnium in zirconium [1-11]. Some authors, e.g. Mortimore and Noble [7], recommend that in order to increase the sensitivity of the determination of hafnium to 0.003%, barium fluoride be added as a buffer, and that evaporation of the samples be carried out from platform type electrodes at a high current strength (30 amps). The spectra were photographed on a grating spectrograph.

Our experiments which were carried out under the conditions suggested by Mortimore, showed that on working with a KSA-1 (KS-55) autocollimating spectrograph, addition of barium fluoride and evaporation using a high current, did not lead to an increase in the intensity of the hafnium line. Some of the increase in the intensity of the hafnium line at Hf 2641.4, when barium fluoride is added, occurs as the result of superposition of the barium line Ba 2641.37. It must be assumed therefore that the sensitivity which Mortimore achieved was mainly the result of the fact that he used a grating spectrograph with a high dispersion, which ensures a favorable relationship between the intensity of the line and that of the background.

The addition of sodium phosphate as a buffer, as recommended by Shvangiradze [8], did not give positive results either.

The requisite increase in sensitivity for the determination of hafnium when a KSA-1 (KS-55) autocollimating spectrograph with a one-lens condenser is used, was achieved by operating under the following conditions:



Calibration curve for the determination of hafnium.

20 mg of zirconium dioxide was mixed with 10 mg of carbon powder and densely packed into the opening of a rounded off graphite electrode (aode). The diameter of the rounded part was 4 mm, and the height of the rounded part was 10 mm, while the crater was 2 mm in diameter and 5 mm deep. Two electrodes filled with sample were prepared in order to get one spectrum. The upper graphite electrode was sharpened to a cone. An arc suppled with a d.c. current of 10 amps was struck between the vertically fixed electrodes. A highly magnified image of the electrodes was projected on to the slit. The central part of the flame was photographed. The slit width was 0.01 mm. Exposure time was 2 minutes. Each spectrum was obtained by superposing two spectra on the same placed on the photographic plate. (Photographic plates "Spectrographic" Type I).

The hafnium line HF 2641.4, the zirconium line Zr 2626.0, and the background near these lines were photometrically measured on the spectra obtained.

Conversion from line blackening to line intensity was carried out, taking into account the background, by using the characteristic curve of the photographic plate.

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Conversion from line blackening to line intensity was carried out, taking into account the background, by using the characteristic curve of the photographic plate.

Determination of the hafnium concentration was carried out by means of a calibration curve constructed within the parameters:

$$\log \frac{I_{\text{Zr-background}}}{I_{\text{Hf-background}}} - \log C$$

A calibration curve for the determination of hafnium dioxide over a concentration range of 0.003 to 0.1% is shown in the diagram.

A primary standard containing 1% hafnium doxide was prepared by grinding up a mixture of zirconium oxide free from hafnium dioxide with hafnium dioxide. The other standard powders were prepared by successive dilution of each of the previous standards with pure zirconium dioxide. For improving the mixing, grinding is carried out with alcohol.

The probable error of a single determination for 0.003 to 0.03% of Hf, amounts to ± 20-30%; for Hf contents greater than 0.03% this error is ± 10.0%.

The method has been used for some years for controlling the freedom of zirconium from hafnium.

We wish to thank A. K. Rusanov for his valuable advice.

SUMMARY

A spectrographic arc quantitative method has been developed for the determination of thousandths of a percent of hafnium dioxide in zirconium dioxide.

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VLADIMIR IVANOVICH PETRASHEN'

(On his seventieth birthday)

On November 22, 1958 the Society of the S. Ordzhonikidze, Novocherkash Polytechnical Institute celebrated the 70th birthday, and 40 years scientific and teaching activity of one of the oldest analytical chemists, Doctor of Chemical Sciences, Professor V. I. Petrashen'.

In the course of the 40 years V. I. Petrashen' has worked as a teacher in various educational establishments of our country, and since 1928 has remained unchanged as the head of the chair of chemistry in the Novocherkask Polytechnical Institute.

V. I. Petrashen' belongs to that number of teacher-scientists who has devoted his whole life to the development of analytical chemistry.

Having started to teach analytical chemistry in 1920 in the Ural University, V. I. Petrashen' as long ago as 1922 1922, published his book"Qualitative Chemical Analysis," which, by 1948 had already reached 6 editions. This book has made the name of V. I. Petrashen' widely known in the Soviet Union and abroad. "Qualitative Chemical Analysis," has been acclaimed by famous scientists: L. V. Pisarzhevskii, I. V, Tananaev, N. N. Efremov, E. S. Przheval'skii, et al.

I. V. Tananaev wrote: Since the well known text book of N. A. Menshutkin on qualitative analysis, no text book on qualitative analysis written by a Russian author for chemistry students has existed in our literature which has proved so popular as V. I. Petrashen's book. The most distinguishing freature of this textbook is that the material within the limits of each analytical group of cations is arranged, not on the basis of the individual cations, as is done by other authors, but on the basis of the reagents used.

V. I. Petrashen's book is an original work which reflects the great scientific erudition of the author and his talent as a teacher.

The second book by V. I. Petrashen' — his textbook "Volumetric Analysis," (1946) — has also become widely known not only in Russia but abroad as well.

Under V. I. Petrashen's direction a vast amount of work has been carried out on an all-embracing study of phosphates from the point of view of their possible applications in analytical chemistry. As a result of these investigations a new method was developed for the analysis of cations of Groups II and III in the prresence of phosphate ions, as well as a systematic analytical scheme for cations which does not involve hydrogen sulfide. In addition, a number of phosphate and phosphato-colorimetric methods have been developed for the quantitative determination of manganese, lead, cadmium, bismuth, and zinc.

Petrashen' was the first to suggest a color reaction for magnesium; this reaction is now called the Petrashen' reaction.

In recent years, under the direction of V. I. Petrashen', research has been carried out on developing new methods of determining tungsten, molybdenum, mercury, chromium, aluminum, thallium, lead, etc. In the school of chemistry headed by Petrashen' new photometric methods are being developed for the determination of certain elements by means of organic reagents, while work is being carried out on the study of complex formation in solution. Petrashen' has published more than 65 scientific papers. Under his direction 24 candidate's these have been carried out and defended. Petrashen' has brought up numerous cadres of analytical chemists who work in many parts of the Soviet Union. Many of his students are leading specialists in the field of analytical chemistry. During the years of his activity, Petrashen' has prepared thousands of highly qualified specialists who are successfully working in various industries of our Socialist country.

The Commission on Analytical Chemistry, the editorial board of J. Anal. Chem. Acad. Sci. USSR, wide circles of Soviet analytical chemists, his comrades and studeents wish V. I Petrashen' long years of fruitful work for science and for the education of the young generation for the glory of our country.

CHRONICLE

THE INTERNATIONAL SYMPOSIUM ON MICROCHEMISTRY

From the 20th to the 27th of August 1958 a symposium on microchemical analysis was held in Birmingham University, England; the symposium was convened by the Midland Section, and the Group on Microchemistry of the Society of Analytical Chemistry of the International Union on Theoretical and Applied Chemistry.

About 400 delegates from 25 countries were present.

The Soviet Union delegation was represented by Corresponding Member of the Acad. Sci. USSR I. P. Alimarin, Prof. R. P. Lastovskii, A. A. Zhukhovitskii, and S. P Motorny.

The symposium was opened by an introductory address given by a member of the Royal Society, Professor Stacey of Birmingham University.

Three sections worked simultaneously at the symposium, while plenary sessions were also held in which reports by famous microchemists were read; about 50 communications by analytical chemists of various countries were given.

All the reports read can be subdivided into the following groups:

Analysis of Organic Materials

A large part of the reports dealt with modernization and development of new methods of elemental analysis (determination of carbon, hydrogen, halogens, sulfur, and also functional groups).

Radiometric Methods in Microanalysis

Worthy of attention were the following : the report by James on "Determination of Traces of Elements in Semiconductors;" the report by Bryant, Spicer, and Osmond on "Determination of Fission Products in Water and Biological Materials;" Gibbons' report on "Determination of Submicrogram Amounts of Cadmium in Superpure Zinc by Neutron-Activation Analysis."

Electrochemical Methods in Microchemistry

The following were interesting communications in this section: Kemul's report on "Separation and Determination of Traces of Organic Materials by a Chromatopolarographic Method." The wide possibilities of the application of the chromatopolarographic method for the determination of organic materials were demonstrated in this report. The author adduced some work published by him previously on this method. Calwood's report on "Polarographic Microanalysis by an Oscillographic Method." This report contained results of the very promising technique of oscillographic comparative titration. For low concentrations (10^{-5}- 10^{-9}M), preliminary electrolysis of the solution is used, after which the amalgam formed is analyzed oscillographically. The method permits determination of a large number of cations. Conditions have been worked out for the determination of certain cations in the presence of large amounts of others. The most rational electrolyte-carriers and complex forming electrolytes for various systems have been established. Ethylenediamine citrate and alkali pyrophosphate are used, after which the amalgam formed is analyzed oscillographically. The method permits determination of a large number of cations. Conditions have been worked out for the determination of certain cations in the presence of large amounts of others. The most rational electrolyte-carriers and complex forming electrolytes for various systems have been established. Ethylenediamine citrate and alkali pyrophosphate is used for the detection of Cu and Fe in cobalt salts. Tsuman's report on "The Use of Polarographic Microanalysis for the Study of Reaction Kinetics."

Professor Semerano gave a review of the possibilities of using polarography in microanalysis.

Chromatographic Microanalysis.

Only two reports were included in this section: "Chromatography of Large Molecules," and "Paper Chromatography of Inorganic Ions."

Physical Methods in Microchemistry

Four reports were given, of these mention should be made of of: "Quantitative Analysis in the Infrared," and "Flame Photometry as applied for Micro Samples and Micro Concentrations."

Organic Reagents in Chemical Analysis

This group of reports was devoted mainly to the study of complexons and metallochromic indicators (the reports of Prshibil, West, and Cheng). Prshibil's report "Research on Chelatometry in Czechoslovakia" was in the nature of a review of work carried out earlier, and partly published in journals.

West's interesting report on "New Reagents in Complexonometric Analysis" was devoted to research carried out in Birmingham University on the synthesis and study of complexons with 5-, 6-, and 7-membered rings, namely: cyclopentamethylenediaminetetracetic acid, cyclohexamethylenediaminetetracetic acid, and cycloheptamethylenediaminetetracetic acid. Of the new complexometric indicators, of interes is the indicator obtained by condensing alizarin with formaldehyde and iminodiacetic acid. The indicator can be successfully used for the determination of fluorine.

A very interesting report was that of Welcher on "Specific and Slective Reagents." This report touched upon a number of important theoretical problems in the application of organic reagents in analysis; in particular, the effect of the addendum on the stability of a complex and its capacity to be extracted by organic solvents.

Techniques of Microchemical Experiment.

This important section of microchemistry was only poorly represented at the symposium — of the 7 reports, of possible interest were the following: "The Practical Application of Chemical Microscopy" (West's report) and "Microdetermination of Physical Constants," (Sobotka's report).

Four Lectures were delivered at the symposium. Prof. Feigl gave a lecture on "Identification of Organic Compounds by Spot Analysis." This lecture contained new, original material. The lecturer gave a number of pyrohydrolysis and hydrolysis reactions of organic compounds, as well as oxidation and reduction reactions, and catalytica reactions which permit detection of various classes of organic materials with reasonable sensitivity.

Prof. Benedetti Pichler's report was devoted to the techniques and methods of ultramicroanalysis. Of interest were new techniques of analysis by a pyrochemical method.

Prof. Lib's lecture "Organic Microanalysis," was of a review nature and contained a long historical introduction. The lecturer considered a number of methods of elemental microanalysis using various oxidizing and reducing agents. Rapid methods of determining halogens and nitrogen, and methods of determining functional groups were considered. All the methods considered were based on a gravimetric or titrimetric finish for the determination of the element or the functional group. Unfortunately, the lecturer did not touch on the question of the use of physicochemical methods such as potentiometry, polarography, etc.

Prof. Belcher's lecture was devoted to the history of the development of microchemical analysis in Birmingham University; in addition, the lecturer also discussed new research on microchemical analysis of organic compounds.

The reports which were read allowed us to get acquainted with a number of new methods of microchemical analysis of organic and inorganic materials. Microchemical methods are at present being successfully developed in many countries including the Soviet Union. The symposium gave an oppor tunity for the latest achievements in this field to be made known.

The symposium also contained an exhibition of the latest laboratory equipment, physicochemical apparatus, chemical reagents, and books as well; the exhibition was organized by English firms.

The visit of the Soviet delegation to the symposium was of great importance in establishing scientific contact with many famous analytical chemists from England and many other countries.

THE FIFTH CONFERENCE OF INDUSTRIAL AND PRODUCTION LABORATORY WORKERS OF KAZAKHSTAN AND CENTRAL ASIA

On October 14-18, 1958 ther was held at Alma Ata the Fifth Conference of the Industrial and Production Laboratory Workers of Kazakhstan and Central Asia, organized by S. M. Kirov the Kazakh State University, Acad. Sci. Kazakh SSR, by the State Scientific-Technical Committee of the Council of Ministers of the Kazakh SSR, and by the Kazakh Section of the D. I. Mendeleev All Union Chemical Society.

A large number of representatives from industrial, production, and scientific research laboratories participated in the conference; they included 150 representatives of more than 60 organizations of the metallurgical and chemical industries, and of laboratories of the geological service, and higher educational establishments in various towns of the Soviet Union.

The conference considered the problems confronting laboratory workers in connection with the decisions of the May Plenary Session of the central Committee of the Communist Party of the Soviet Union regarding the increased development of the chemical industry, and in connection with the program of the development of the social economy of the USSR during 1959-1965.

The conference was divided into four section: analytical, spectrographic analysis, organic technology, and the technology of mineral materials, and a total of 94 reports were read.

As a result of the exchange of opinion, on the reports that were heard, the conference adopted a resolution regarding the further development of scientific-research work in analytical chemistry and spectrographic analysis, and on questions relating to the improvement and organization of the work of factory and production laboratories. In particular, the conference recognized the basic problems of developing express and automatic methods of analysis, methods for the determination of small amounts of elements, phase analysis methods, and the development and introduction of new methods of spectrographic and flame-photometric analysis and also work on the automation of the ignition of samples and registering radiation.

A number of suggestions related to the issue of new apparatus, to increasing the issue of literature, and to the organization of courses for increasing the qualifications of workers in industrial and production laboratories, to questions of improving the training of analytical specialists within the system of the Ministry of Higher Education, and to other questions relating to the organization and improvement of the work of industrial and production laboratories.

SCIENTIFIC TECHNICAL CONFERENCE ON MODERN METHODS OF ANALYTICAL CONTROL IN BASIC CHEMICAL INDUSTRY

On 13-15 November 1958, there was held at Moscow a scientific-technical conference on modern methods of analytical control in basic chemical industry; 174 representatives from 87 enterprises, scientific-research, educational, and planning institutes took part.

On the basis of the reports which were read and on the discussions which followed the conference established that during recent years a considerable number of new chemical and physicochemical methods of analysis had been introduced into the practice of analytical control, in particular, complexonometric, and photometric, spectrographic, chromatographic, polarographic, potentiometric, mass-spectrometric, radiometric, and luminescence methods.

As a result of the discussions, the conference regarded it as essential to increase theoretical studies in order to increase the sensitivity and selectivity of chemical reactions, and also to intensify work on the search for new, sensitive reagents suitable as a basis for developing continuously operating control apparatus.

Particular attention was devoted to the necessity of developing work on the construction of new apparatus and the organization of the series production of apparatus which have proved themselves in practice.

It was decided that it is desirable to organize specialist laboratories to develop new analytical reactions and reagents for the development of rapid methods of analysis for organic and inorganic materials, and for particularly pure materials. It was suggested that the number of scientific-research laboratories based, on a number of large enterprises in basic chemical industry should be increased. The necessity was emphasized of strengthening the link between the central industrial laboratories of chemical enterprises with the scientific-research institutes and the chemistry faculties of educational establishments.

A number of resolutions adopted by the conference related to the organization of courses and seminars for improving the qualification of the workers in the central industrial laboratories, and also to the issue of sufficient textbooks on the methods of analysis for the various products of the chemical industry.

REVIEWS AND BIBLIOGRAPHY

"THE CHEMISTRY OF METAL CHELATE COMPOUNDS, by A. E. Martell and M. D. Calvin

Die Chemie der Metallchelatverbindunge, Martell A. E., Calvin M. VI, 576 pp., Verlag Chemie, G. M. B. H. Weinheim/Bergstr., 1958.

Chelate compounds are of great importance for almost all branches of chemical science. They play an outstanding role in analytical and preparative chemistry, and also in various branches of industry. A multitude of valuable, sensitive and selective methods of titrimetric, photometric, electrometric, extraction and ion exchange analysis is based on the use of chelate compounds. They enable complex problems in the separation of radioactive mixtures to be solved, and enable new, technically economic methods of controlling chemical processes to be created, processes such as water softening, flotation , emulsion polymerization, fiber dyeing, conservation of detergents, stabilization of peroxides and vitamins, purification of lubricating oil and chemical reagents, etc. Accordingly, the appearance of an American edition of the monograph under review (1952) and its German translation (1958) must be regarded as an important event in scientific chemical literature.

Results of many years work by Martell and Calvin in the field of the chemistry of chelate compounds are collected in this monograph. This was the first book in world literature in which the various published data on chelate chelate compounds were fairly completely systematized and discussed. In their book the authors have not made it their aim to give an exhaustive review of the existing literature, to give a complete survey of all known chelate compounds, or to enumerate all their applications. What they did was to endeavour to explain the general principles of the chemistry of chelate compounds, and to show by means of numerous examples the importance of these compounds for science and industry, so as to lead the reader on to search for new compounds and new applications.

Martell and Calvin's book is divided into 10 chapters.

The first chapter (16 pages) contains definitions of the basic terms, while the questions of the formation of chelate compounds are treated in a very general form, their importance is also noted.

The second chapter (52 pages) is a review of the methods used for establishing the formation of chelate compounds, and reflects the position in this field towards the end of the forties. More recent work, with few exceptions, is not considered. Chief attention is given to spectrophotometric, conductometric, potentiometric, polarographic, x-ray spectrographic, and some other methods.

In the next chapter (55 pages) the use of some of the methods listed above, as well as of some other methods, for the quantitative evaluation of the stability of chelate compounds is discussed. Such data is of great importance for calculating the various equilibria in analytical chemistry and other branches of chemistry.

The fourth and fifth chapters (63 pages) are devoted to a discussion of the significance of the structure of chelate forming materials and of metal ions for the formation of chelate compounds. Considerable attention is given to the effect of various factors on the stability of these compounds. The problem of the specificity and selectivity of analytical reagents is also touched upon.

In the 31 pages of the sixth chapter a vast amount of material relating to the nature of the chemical bond between the complex-forming ion and the donor atoms in chelate compounds is set forth. Most attention is focussed on the numberous magnetic methods which open up the greatest possibilities for determining the nature of the bond.

The seventh chapter (85 pages) is a review of the stereochemistry of chelate compounds, naturally this cannot pretend to be of exhaustive thoroughness.

The various catalytic effects of chelate compounds are discussed in the 86 pages of Chapter VIII.

The ninth and tenth chapters (73 pages) are devoted to numerous examples of the uses of chelate compound for ion exchange and extraction separation of mixtures is considered in fair detail in chapter nine.

The book finishes with a large table of stability constants for 600 chelate compounds (56 pages) with references to the original literature. The table is not up to date. The book is provided with author and subject indices; the tables and references to original work are well documented. The text includes many structural formula and diagrams. The book is printed and bound very well. The convenient arrangement of material and its clarity make it a very easy book to persue. The fairly detailed treatment of the most important question in this field make this book a valuable reference book for scientific-research, analytical, and industrial laboratories.

Since its first appearance in an American edition in 1952, this book has been widely acknowledged. The edition of a German translation will ensure that it will become even more widely known.

We can only regret that the German edition is an exact reproduction of the American original. The book would undoubtedly benefit if its translation into German had been accompanied by the inclusion of research work in the chemistry of chelate compounds published during 1951-1958, including that by Martell and Calvin, even if it were only the most important work during that period that room could be found for. During this period interesting work has been carried out on the connection between the structure of a reagent and its analytical properties, and important theoretical research has been published which opens up methods for forecasting the conditions for carrying out analytical determinations, while methods for determining the composition and evaluating the stability of chelate compounds have been develped further. In addition, a large amount of work has been carried out on the study of the composition and properties of many chelate compounds. During this period also, new methods for establishing the equivalence point have been developed (heterometric, haigh-frequency) which enhance the analytical value of chelate compounds. The number of analytical applications of these compounds for masking, for varying the oxidation-reduction potential and, for extraction and ion exchange separation of mixtures, has increased considerably. These achievements should be included in a new edition.

All the same, even in its present form, Martell and Calvin's book is of great scientific value for a wide circle of analytical chemists. The book satisfies the primary needs of research workers on the chelate compounds of metals. An enlarged Russian edition of Martell and Calvin's monograph will undoubtedly be greeted with great interest by Soviet chemists.

A. I. Busev and N. G. Polyanskii

A NEW REAGENT FOR SCANDIUM

A new reagent for the photometric determination of scandium — "Sul'fonazo" — has been synthesized at the All-Union Scientific Research Institute of Chemical Reagents (IREA).

This reagent is more selective than alizarin S, quinalizarin, and arsenazo while being approximately equal to them in sensitivity. Scandium can be determined in the presence of considerable amounts of yttrium and the rare-earths. Satisfactory results are obtained during the determination of scandium in silicate rocks, and coal-ash. The reagent possesses advantages over other reagents.

Organizations and enterprises wishing to test the new reagent can get a free sample of it, together with instructions for its use, on applying to the following address: Moscow Zh-33, Samokatnaya Ul., D-4-a-Institute of Chemical Reagents.

Sul'fonazo is not at the moment being produced on a factory scale, and in order to establish whether it is worth organizing its production, the Institute of Chemical Reagents urgently requests all those organizations and enterprises who receive samples of the new reagent to let the Institute know about the practical value of the reagent within a two-month period.

THE COLOR OF INTERCOMPLEX AND CYCLIC SALTS

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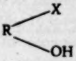
The theoretical bases of photometric analysis and the mechanism of color reactions have still not been studied sufficiently [1, 2]. Despite the fact that in recent years, mainly thanks to the work of Soviet scientists (A. K. Babko, L. M. Kul'berg, V. I. Kuznetsov, I. M. Korenman, and N. P. Komar'), many important contributions have been made to the understanding of the mechanism of color reactions, to the choice of the optimum conditions for carrying them out, to making new highly sensitive organic reagents, and to studying the composition of colored complexes in solution, the question of clarifying the theory of organic reagents still remains untouched. Thus, up to now, these is still no unanimous view on the relation between the color of complex compounds in solution and their composition [3], while the physicochemical interpretation of color changes during complex formation with colored organic reagents is still to come. Recently, Kuznetsov proposed the so called hypothesis of intermolecular dissociation [3-7] for this purpose; unfortunately, this hypothesis does not have sufficient theoretical backing and contradicts many known facts.

According to this hypothesis the change in color which occurs during formation of a cyclic salt between a metal cation, which does not possess an intrinsic color, and a colored organic reagent of the type  (where X= —OH, —COOH, = CO, = O, etc.), can be explained by intermolecular dissociation of one of the bonds formed between the element and the reagent , as a consequence of which the color of the latter approximates to the color inherent in the usual ionic state of the reagent. This approximation of the color of the complex to that of the reagent in its usual ionic state occurs in alkaline solutions, the approximation being the closer the more fully intercomplex dissociation is manifested .

On this basis the assumption was made that the extent of intermolecular dissociation of a complex cyclic salt formed by a metal ion not possessing a chromophoric action, with a colored reagent, can be quantitatively evaluated by choosing the appropriate concentrations of the undissociated and dissociated forms of the reagent so that their sum reproduces the color of the complex cyclic salt both with respect to shade and intensity [5].

Nevertheless, during a study of color reactions connected with the formation of cyclic salts , we established a number of facts which are incompatible with the hypothesis of intermolecular dissociation. A discussion of these facts , and their explanation from the point of view of modern polarization theory regarding the nature of the chemical bond, form the major content of the present article.

Comparative Study of the Light-Absorption Curves of Solutions of Reagents and their Complex Cyclic Salts

A study of the light-absorption curves of solutions of cyclic salts showed that they differ strongly from the light-absorption curves of solutions of reagents, the color of which coincides visually with the color of the solutions of the complexes. This coincidence of colors can be achieved in two ways.

An alkaline solution of the reagent is placed in one cell with a layer thickness of 10mm, while an acid solution of the reagent is placed in another cell. The total concentration of the reagent in both cells is a constant.

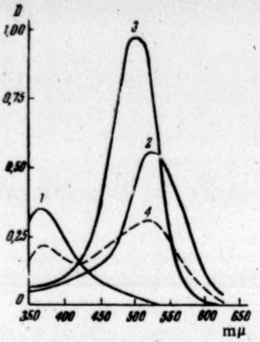


Fig. 1. Absorption curves for solutions of 3,4-dihydroxyazobenzene-4'-sulfonic acid and its cyclic zirconium salt. SF-4 spectrophotometer; cell with layer thickness 10 mm; reference solution, water. In all cases the reagent concentration was 7.4 mg/liter. 1) Reagent in 0.05 N HCl; 2) reagent in 0.05 N NaOH; 3) cyclic zirconium salt (Zr was taken in a 2.5-fold molar ratio to the reagent in order to exclude dissociation of the complex formed); reagent in 5% Na_2CO_3 solution, the color of which coincided visually with the color of the solution of the cyclic zirconium salt.

The concentrations of the alkaline and acid solutions are chosen so that on examining both cells placed one behind the other, the color coincides visually with the color of a solution of complex placed in the same cell; behind this is placed still one more cell filled with water.

The same effect can be produced by choosing the pH of the reagent solution so that its color coincides with the color of the solution of the complex.

It was found even in those few instances when it was possible to match visually the color of the solution of the complex with the total combined color of the undissociated and dissociated forms of the reagent that the nature of the light absorption curves of such mixtures in the given instance, indicate two colored substances in solution, while the solutions of the complexes are characterized by light-absorption curves which are typical for a solution of one colored material.

As an example there is given in Fig. 1 the absorption curves for a solution of the complex of zirconium with 3,4-dihydroxyazobenzene 4'-sulfonic acid, and for solutions of the reagent itself in acid and alkaline media, as well as for a solution of the reagent where the color of the solution matches a solution of the zirconium complex.

Similar results were also obtained with other cyclic salts of 3,4-dihydroxyazobenzene-4'-sulfonic acid, in particular, with the aluminum, gallium, germanium, and beryllium salts.

Other reagents behave in the same way, e. g. alizarin S (Fig. 2), 2,4-disulfobenzaurine-3',3''-dicarboxylic acid (Fig. 3).

Thus, by comparing the light-absorption curves of solutions of the complexes and of solutions of the reagents which match in color, it follows that in the case of solutions of reagents containing dissociated and undissociated forms of the reagents, each of these forms is independently reflected in the light-absorption curves, while in the case of solutions of the complexes, the dissociated and undissociated forms of the reagent are absent (under conditions where the reagent is completely bound as the complex, this being achieved by adding sufficient excess of the element). Instead of them there appears a new form which is intermediate between the dissociated and undissociated forms.

Levin [8] while studying the absorption spectra of cyclic complex compounds formed between ketoesters and multivalent metals, also found that in solutions of these cyclic complexes, the enol and ionic forms are absent. According to the light-absorption curves, these complexes occupy an intermediate position between the undissociated enols and their ionic state.

The absence of both the ionic form and the undissociated form of the reagent in solutions of the complex cyclic salts, is incompatible with the ideas regarding intermolecular dissociation of these salts developed by Kuznetsov [4,5].

The Color of Cyclic Salts in Solution and in the Solid State

The colors of cyclic salts in solution and in the solid state, as a rule, coincide quite well each other. At the same time the colors of the free reagents and their cyclic salts strongly differ from each other, independently of the form they are compared in. In Table 1 are given the colors of a number of known organic reagents and their cyclic salts both in solution and in the solid state. In those cases where in the solid state the deep tone of the color (blue, green) and its exceptionally high intensity complicate its determination, the dry preparations were ground with 50-200 times their amount of NaCl.

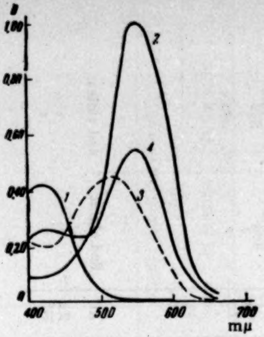


Fig. 2. Absorption curves for solutions of alizarin S and its cyclic zirconium salt. SF-4 spectrophotometer; cell with layer thickness 10 mm; reference solution, water. In all cases the reagent concentration was 18 mg/liter. 1) Reagent in 0.05 N HCl; 2) reagent in 0.05 N NaOH; 3) cyclic zirconium salt (Zr was taken in a 2.5-fold molar ratio to the reagent to exclude dissociation of the complex formed); 4) reagent solution, whose color matches visually the color of a solution of the cyclic zirconium salt.

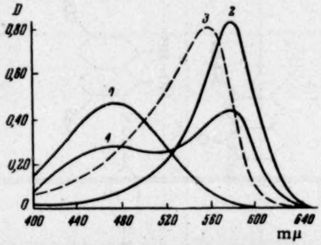


Fig. 3. Absorption curves for solutions of 2,4-disulfobenzaurine-3',3''-dicarboxylic acid and its cyclic zirconium salt. SF-4 spectrophotometer; cell with layer thickness 10 mm; reference solution, water. Reagent concentration in all cases 25 mg/liter. 1) Reagent in 0.05 N HCl; 2) reagent in 0.05 N NaOH; 3) cyclic zirconium salt (Zr was taken in a 2.5 fold molar ratio to the reagent for excluding dissociation of the complex formed); 4) reagent solution whose color matches visually the color of a solution of the cyclic zirconium salt.

As additional evidence to that given in Table 1 it should be pointed out that numerous metal-containing dyes (palatins, cibalans, neolans) which are soluble complex compounds of dyes with metals, color fabrics the same color that they exhibit in solution. Metal-containing dyes both in the solid state, on fibers, and in solution have the same colors. It should also be added that many color spot reactions on paper, and also developed paper chromatograms after drying, preserve their original color. Exceptions are so rare and insignificant, that the existence of such a regularity does not lead to any doubt.

The facts adduced are also incompatible with ideas regarding intermolecular dissociation, according to which the color of cyclic salts in solution should differ from their color in the solid state, in which, as is well known, neither ordinary nor intermolecular dissociation occurs.

Steric Hindrance

The very existence of cyclic salts, in which the metal ion is connected simultaneously with two functional groups directly by bonds having a definite length and direction in space, excludes the possibility of intermolecular dissociation. Even if one were to assume that, despite this obstacle, the ions were displaced in space, and in this way intermolecular dissociation were achieved, then, in this case, the cyclic salt containing the metal ion connected by only one functional group should not differ in any way from the ordinary noncyclic salt. However, the properties of cyclic salts show that they possess, in comparison with the corresponding noncyclic salt, exceptionally high stability. In this connection therefore the assumption of intermolecular dissociation of cyclic salts on the basis of one of two bands should be discarded.

Chemical Properties of Addenda in Complex Salts and in the Ionic State

It was pointed out recently in a number of papers [9-12] that there is an increase in the reactivity of certain organic compounds when in the form of their cyclic salts during azo coupling and nitrosation. According to the intermolecular dissociation hypothesis, this phenomenon would be explained by the presence of an intermolecular ionic state coinciding with the usual ionic state of the same organic compounds (chromotropic acid, pyrocatechol, salicylic acid) the amount of the ionic state being the same in both cases. However, in these papers it was established that there is a major difference between the chemical properties of organic compounds in the form of their cyclic salts, and in the usual ionic state. Thus, chromotropic acid, and in particular pyrocatechol, being in the ionic state in alkaline solutions, are readily oxidized by diazo compounds, as a result of which the corresponding azo compounds are either not formed completely or are formed in insignificant yields. In the case of cyclic salts the reverse is true; oxidation processes are suppressed giving way to azo coupling and nitrosation reactions.

TABLE 1

Colors of Some Organic Reagents and their Cyclic Salts in Solution and in the Solid State

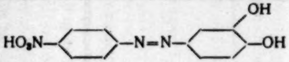
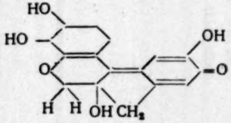
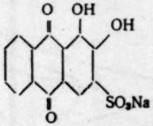
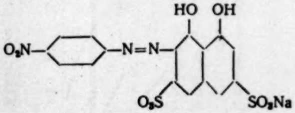
Reagent				Cyclic salt of the reagent		
		Color		With the element	Color	
Designation	Formula	In solution	In the solid state*		In solution	In the solid state*
3,4-Dihydroxyazobenzene-4'-sulfonic acid		Yellow	Yellow	Zr Hf Th	Red « «	Red » »
Hematein		Red	Red	Al	Blue	Blue
Alizarin red S		Yellow	Yellow	Pb Al Th Zr	Rose Red » »	Rose Red » »
Chromotrop 2B		Orange-red	Orange-red	Al Zr Hf	Red violet » »	Red violet » »

TABLE 1 (Continuation)

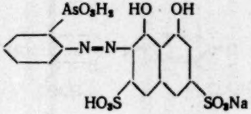
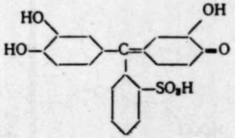
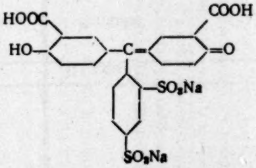
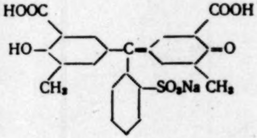
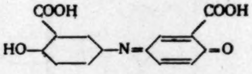
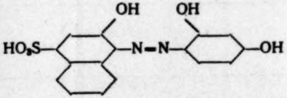
Reagent				Cyclic salt of the reagent		
		Color		With the element	Color	
Designation	Formula	In solution	In the solid state		In solution	In the solid state
Arsenazo		Red	Red	Be Al Th Zr	Rose » Blue-violet »	Rose » Blue-violet »
Pyrocatechol violet		Yellow	Yellow	Be Pb Zn Al Th Zr	Blue » » » » »	Blue » » » » »
2,4-Disulfobenzaurine-3',3''-dicarboxylic acid		Yellow-orange	Yellow-orange	Be Al Zr Th	Rose Violet » »	Rose Violet » »

TABLE 1 (Continuation)

Reagent				Cyclic salt of the reagent		
		Color		with the element	Color	
Designation	Formula	in solution	in the solid state		in solution	in the solid state
Eriochromcyanine		Orange	Orange	Al Zr	Violet »	Violet »
4-Phenolindophenol-3,3'-dicarboxylic acid		Red-orange	Red-orange	Be Zn Al Zr Th	Blue » » » »	Blue » » » »
2,4-Dihydroxybenzene-1-azo-1 -2-hydroxynaphthalene-4-sulfonic acid		»	»	Zr Hf Th	Rose » »	Rose » »

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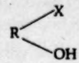
* The colors of the reagent in the solid state were determined after evaporating solutions to dryness. The pH of the evaporated solutions corresponded with the pH of the solutions of the cyclic salts the colors of which were compared.

This is explained by the fact that the electron pair on the phenolic oxygen atom in the cyclic salt, cannot switch over freely to the carbon atom as a result of its interaction with the neutral atom of the metal carrying a positive charge. The same is true for the suppression of decarboxylation during nitrosation of cyclic salts of salicylic acid [12]. If there actually were a similarity in the behavior of cyclic salts and alkaline solutions of the addenda themselves, there would be no need to use cyclic salts for facilitating syntheses which are difficult to carry out. Instead of cyclic salts, in the appropriate cases, it would be possible to use alkaline solutions of those same addenda, in which normal ionic state is manifested to the same extent as in cyclic salts.

Such a substitution is, however, out of the question. Thus, the calcium salt of chromotropic acid is readily coupled with 1-diazo-2-naphthol-4-sulfonic acid to give the corresponding azo compound, while under the same conditions, ordinary alkaline solutions of chromotropic acid at the same pH values, as a result of an increased tendency to oxidation, also react with the same 1-diazo-2-naphthol-4-sulfonic acid but without formation of the azo compound. [11].

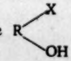
Thus, these differences which have been established between the chemical properties of addenda taken in the form of their cyclic salts, and of the same addenda in alkaline solutions, clearly contradict the hypothesis of intermolecular dissociation of cyclic salts.

Polarization Considerations

In accordance with modern ideas regarding the nature of the chemical bond [13-17], the ionic state of a reagent of the type  in an alkaline medium is the limiting case of the polarization of the O-H bond. In acid solutions such a reagent is found, as a rule, in a molecular form, in which the bond O-H is almost unpolarized. Replacement of the H atom by a metal which increases the polarity of the bond, leads to the appearance of a partial negative charge on the oxygen atom.

It is known that the changeover of colored organic compounds into an ionic state is accompanied by a change in their color [18]. It is true with the changeover of the colored organic material into an ionic state, the color does not change in those cases where the functional group — as the result of whose dissociation the material changes into the ionic state — is not conjugated with the chromophoric system of the colored material. If the bond in a molecule of a colored organic compound which can dissociate is polarized, then the color of such a compound will not coincide with the color of the same material either in the ionic or molecular form. Polarization of the bond to the same extent as the colored material approaches the ionic state, shows a corresponding effect on its color also [19].

Thus, Kul'berg [20] is of the opinion that if the polarity of the complex compound formed is greater than the polarity of the reagent itself, the depth of color will increase; while if the polarity of the compound formed is almost the same as the polarity of the reagent, then there will be hardly any change in color; and, if the new group depresses the polarity of the molecule then the color will be less intense.

Thus, the reason for the change in color of colored organic reagents of the type  which occurs during complex formation with metal cations not possessing an intrinsic chromophoric action, is not intermolecular dissociation of the cyclic salts, but the increase in polarity of the colored organic reagent.

Since dissociation into ions is the limit of the bond polarization, then in accordance with this, the change in color determined by the breakdown of the reagent into ions is always greater than the change in color which occurs during complex formation, as long as no additional changes occur in the structure of the reagent itself.

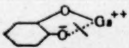
From the point of view of polarization considerations the similarity between the colors of cyclic salts in solution and in the solid state becomes understandable. The reason is that in both cases the bonds are polarized to the same extent.

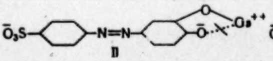
Polarization considerations are also in good agreement with the nature of the absorption curves for solutions of cyclic salts, which indicate the absence of both dissociated and molecular forms of the reagent.

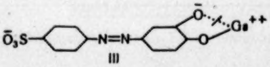
At the same time that intermolecular dissociation cannot be reconciled with the higher stability of cyclic salts as compared with the corresponding simple salts, from the point of view of bond polarization such an increase in stability would be necessary, since in this case the metal ion is connected with the reagent not by one but by two bonds simultaneously.

As indicated already, the hypothesis of intermolecular dissociation of cyclic salts presupposes dissociation along only one of the two bonds of the metal with reagent [4]. This assumption was made on the grounds that dissociation along two bonds simultaneously is incompatible with the existence of the cyclic salt itself [4]. Such a difference in the nature of the two bonds can be justified to some extent only in those cases where both the functional groups of the reagent forming the bond with the same metal ion are different. When these groups are completely identical, as for example in the cyclic gallium salt of pyrocatechol, the structure of which according to Kuznetsov [4] is that given in form I, then the assumption regarding the inequality of the two completely similar bonds contained in this cyclic salt, an assumption which Kuznetsov made without any proof, cannot be justified. The work of Calvin and Wilson [21] confirm that these bonds are of equal value.

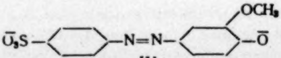
Further, in choosing one of the two structures of the gallium complex (II or III), formed in weakly acid solution during the interaction

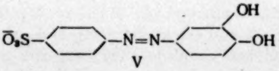

I

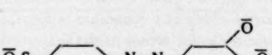

II


III

of 3,4-dihydroxyazobenzene-4-sulfonic acid with Ga^{3+} ions, Kuznetsov proceeds on the grounds that the color of solutions of the complex formed is closer to the color of the alkaline solutions of 3-methoxy-4-hydroxyazobenzene-4'-sulfonic acid (IV), and not of the acid (V) or alkaline (VI) solutions of 3,4-dihydroxyazobenzene-4'-sulfonic acid. Moreover, the dissociation of


IV


V


VI

the hydroxyl group in position 3 has an insignificant effect on the color, this is taken as evidence against structure III. On this basis structure II was chosen.

However, solutions of the cyclic gallium salt of 3,4-dihydroxyazobenzene-4'-sulfonic acid proved to be deeper colored than solutions of IV. According to the intermolecular dissociation hypothesis solutions of the gallium cyclic salt should not have a deeper color than solutions of IV, even if there was complete intermolecular dissociation of one of the two bonds. Accordingly, the hypothesis of intermolecular dissociation is not confirmed in this case even by the example cited by V. I. Kuznetsov. This difference between the colors of solutions of the cyclic gallium salt (II) and of an alkaline solution of 3-methoxy-4-hydroxyazobenzene-4'-sulfonic acid (IV), which contradicts the hypothesis of intermolecular dissociation, can be explained on the grounds that in the cyclic gallium salt (II) there is a substituent OGa^{2+}, which gives rise to a somewhat deeper color than the substituent OCH_3 in compound (IV).

From the point of view of the polarization of the bonds there is no need in the case of the cyclic gallium salt of pyrocatechol (I) to make a compulsory distinction between the two similar bonds formed by the metal ion, in order to explain its enhanced chemical activity. In the given instance, these bonds are polarized to the same extent. In other cases they may be polarized to varying extents, as a consequence of inequalities in the functional groups which directly form the bonds with the metal ion. Recognition of the polarity of both bonds in the cyclic gallium salt formed during the interaction of 3,4-dihydroxyazobenzene-4'-sulfonic acid with Ga^{3+} ions, makes it easy to explain the somewhat more reddish shade of the color of solutions of the cyclic gallium salt in comparison with that of alkaline solutions of 3-methoxy-4-hydroxyazobenzene-4'-sulfonic acid (IV). In actual fact, depending on the degree of polarization of both bonds of the reagent with Ga^{3+} ions, the color of a solution of the cyclic salt can be either darker or lighter than the color of an alkaline solution of 3-methoxy-4-hydroxyazobenzene-4'-sulfonic acid. From the point of view of bond polarization, the possible limits of the color changes of solutions of cyclic salts are extended: the colors of solutions of the cyclic salts may change (depending on the metal ion) from the color of the reagent itself in acid solutions to the color of its alkaline solutions.

TABLE 2

Colors of the Sodium and Potassium Salts of Nitrophenols [22]

	Sodium salts	Potassium salts
o-Nitrophenol	Intense yellow	Red
p-Nitrophenol	Almost colorless	Yellow

The hypothesis of intermolecular dissociation of cyclic salts cannot explain the change in color of reagents forming simple salts but not cyclic salts. Changes in color during formation of simple compounds is the result of bond polarization. From polarization considerations it is easy to explain the differences in color of a number of simple salts, e. g., the sodium and potassium salts of o- and p-nitrophenols (see Table 2). K$^+$ ions form bonds which are more polarized than those formed by Na$^+$ ions, as a result of which the potassium salts of o- and p-nitrophenols are more deeply colored than the corresponding sodium salts.

The coincidence of the red color of an alkaline solution phenolphthalein with the color of its solid salt [23] found in the undissociated form a coincidence which cannot be explained on the basis of the theory of ionic colors is readily explained by the fact that in the solid salt of phenolphthalein the bond with the metal is strongly polarized, as a result of which it approximates to the ionic state of phenolphthalein with respect to its effect on color.

On this basis of polarization considerations, it also becomes clear why the color which develops during the absorption of reagents of the type ROH on hydroxide precipitates and on the insoluble salts of a number of metals are similar to the colors of aqueous solutions of these reagents on addition of alkali. From this it follows that absorption is equivalent, to a certain extent, to the electrolytic dissociation of these reagents, when a proton splits off and a phenolate is formed. However, the maxima of the absorption bands of the absorbed phenols do not coincide accurately with those for the phenolate ions, and show a characteristic dependence on the electrostatic field on the surface of the crystal lattice. Thus, during the adsorption of p-nitrophenol, thymolphthalein, and alizarin on BaF_2, and CaF_2 the color change is stronger in the case of BaF_2 than CaF_2 [24].

The hypothesis of intermolecular dissociation of cyclic salts cannot explain the change in color of adsorbed reagents. Being fundamentally unsound it can only show a negative influence on the further development of the theoretical bases of photometric analysis. In view of this it should be replaced by polarization considerations which have received general recognition in modern chemistry.

As for the designation of polarization bonds, then in those cases where it is necessary, the symbols generally accepted at present should be used [13, 25, 26], i. e., the shift of an electron pair should be designated either by means of straight or curved arrows, or by the symbols for atoms marked with signs of incomplete (partial) charges.

SUMMARY

It has been shown that the hypothesis of intermolecular dissociation of cyclic salts which presupposes the dissociation of one of the two bonds of the cyclic salt with formation of an intermolecular ionic state, has no factual basis.

It has been found that the nature of the light absorption curves of solutions of cyclic salts, the coincidence of their color in solution and in the solid state, and the enhanced reactivity of the cyclic salts as compared with that of the free reagents under identical conditions, are all incompatible with the hypothesis of intermolecular dissociation of cyclic salts.

It has been shown that all the specific properties of cyclic salts can be satisfactorily explained on the basis of the polarization of the bonds formed between the organic reagent and the metal ion.

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SPECTROPHOTOMETRIC STUDIES OF REACTIONS WHICH ARE IMPORTANT IN ANALYTICAL CHEMISTRY

COMMUNICATION 2. COMPLEX COMPOUNDS FORMED BY COPPER IONS WITH SODIUM 2-NITROSO-1-NAPHTHOL-SULFONATE*

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The A.M. Gor'kii Kharkov State University

Substituted 1-nitroso-2-naphthol and 2-nitroso-1-naphthol are finding wide application in analytical chemistry, particularly in photometry. Thus, nitroso-R-salt (sodium 1-nitroso-2-naphthol-3,6-disulfonate) is used for the photometric determination of cobalt [1]. The same reagent has been proposed for determination of iron [2]. Another compound, sodium 2-nitroso-1 naphthol-4-sulfonate**, as Sarver [3] showed in 1938, also forms colored compounds with cobalt, iron, copper, and nickel. This reagent was again mentioned in a number of review articles [4-6]. Recently a paper appeared in which a method was described for the photometric determination of cobalt by means of this material [7]. It is clear from these papers that nitroso-N-salt like the nitroso-R-salt can be used for determining cobalt.

Earlier we studied the composition, optical properties, and stability of the compounds which nitroso-N-salt forms with cobalt [8] and nickel [9]. Cobalt is found in the trivalent state in the complex compounds formed with both nitroso-N-salt and nitroso-R-salt, and forms CoR_3 [10,11]. With nickel, two compounds NiR and NiR_3 are formed, although the possibility of the formation of an intermediate compound NiR_2 cannot be overlooked [9]. The present article contains results of a study of the complexes of copper with nitroso-N-salt.

Sodium 2-nitroso-1-naphthol-4-sulfonate was prepared according to Witt and Kaufman's procedure [12], and in addition was recrystallized twice from water and then washed with alcohol. The absorption curves of solutions with equal concentration of material, after the first and second recrystallization, coincided with each other exactly. Cupric sulfate was crystallized twice. The copper concentration of the solutions was determined iodometrically. The optical density was measured on a spectrodensograph [13], while the pH was controlled potentiometrically by means of a glass electrode. A definite pH value was established by means of HCl or NaOH, in order to avoid the necessity of taking into account the interaction of copper ions with the components of buffer mixtures.

In Fig. 1 are given the absorption curves for solutions of Cu^{2+} ions and nitroso-N-salt in the proportion of 1: 3, at various pH values. The initial concentration of copper $C_{Cu^{2+}} = 2.1 \times 10^{-4}$ M/liter. Curves 1 and 9 almost coincide with the absorption curves of nitroso-N-salt at the corresponding pH values. At pH 10, after removal of the precipitate, the absorption curve of the filtrate coincides exactly with the absorption curve of the nitroso-N-salt of the same concentration and at the same pH. This indicates complete breakdown of the complex compound. It is interesting to note that the analogous complex with nickel is completely stable under the same conditions [9]. As becomes clear later, this is not connected with the lesser stability of the copper complexes, but with the higher hydrolysis constant of the copper ions.

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* For Communication 1 see J. Anal. Chem. 9, 151 (1954) [C.B. Translation].

** In order to shorten the name of this compound we shall henceforth call it "nitroso-N-salt" and designate it by the arbitrary sign RH.

Determination of the stoichiometric coefficients in the equation for the interaction of nitroso-N-salt with copper ions was carried out by the Ostromyslensky-Job method [14, 15, 16]. Experiments were carried out at pH 2, 3, 4, 5 and 6.5, 2-3 parallel determinations being made. Measurements were made at 540, 520, 500 and 480 mμ. In the first series the initial equimolar solutions had a concentration of copper and nitroso-N-salt of 1.2×10^{-3}, while in the second series the concentration was 3.0×10^{-3} M/liter. In Fig. 2 are given as an example typical "ΔD-mixture composition" curves. As is evident from the curves, the ratio of the stoichiometric coefficients at pH 2.0 and 3.1 is 1: 1; while at pH 4.0 the maximum on the curve is diffuse and the ratio approximates to 1: 2; at pH 5.0 and 6.5 the ratio is 1: 3.

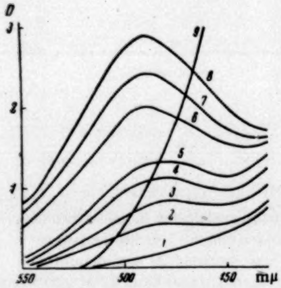

Fig. 1. Absorption curves for solutions containing 2.1×10^{-4} M/liter of Cu^{2+} ions and 6.3×10^{-4} M/liter of nitroso-N-salt, at various pH values: 1) pH 1.95 2) pH 2.50; 3) pH 3.00; 4) pH 3.50; 5) pH 3.95; 6) pH 5.00; 7) pH 6.10; 8) pH 7.30; 9) pH 10.

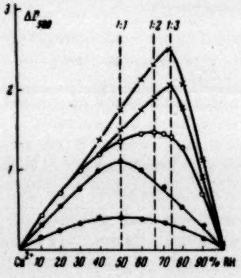

Fig. 2. Curves obtained by the Ostromyslensky-Job method; $C_{Cu^{2+}} = C_{RN} = 1.2 \quad 10^{-3}$ M/liter; λ=500 mμ; l = 1 cm.
-●-●- at pH 2.0 and 3.1;
-○-○- at pH 4.0;
-x-x- at pH 5.0 and 6.5.

The following experiments were carried out in order to investigate the equilibrium in acid solutions at pH < 4. Under these conditions, apparently, one has to take into account the dissociation reaction based on the hydroxyl group of the nitroso-N-salt

$$RH \rightleftharpoons R^- + H^+, \tag{1}$$

the constant K_1 of which we determined earlier and was found to be 8.2×10^{-7} [17], and the reaction of the formation of the complex

$$Cu^{2+} + R^- \rightleftharpoons CuR^+ \tag{2}$$

with a constant K_2'.

The over-all reaction is expressed by the equation:

$$Cu^{2+} + RH \rightleftharpoons CuR^+ + H^+ \tag{3}$$

the equilibrium constant of which

$$K_I = K_1 \cdot K_2' = \frac{[CuR^+][H^+]}{[Cu^{2+}][RH]} \tag{4}$$

In order to calculate the molar extinction coefficients of the complex CuR^+ and the value of K_I, the optical density of solutions was measured in which $C_{Cu_2^+} = C_{RH}$, $C_{Cu^{2+}}$ being varied within the limits $1.2 \times 10^{-3} - 3.0 \times 10^{-4}$ M/liter. Measurements were made at pH 2.15. Table I contains the results obtained for the optical density of the solutions at four wavelengths. The molar extinction coefficients were calculated on the basis of these results, using the formula suggested by Komar' [18]. For the case where the ratio of the stoichiometric coefficients in the reaction is equal to 1: 1, the formula is of the form

$$\epsilon = \frac{1}{l} \cdot \frac{D_1 - nD_2}{C_1 - nC_2} \tag{5}$$

where D_1 and D_2 are the measured optical densities of solutions in which the copper ion concentrations are C_1 and C_2; l is the thickness of the layer in cm; $n = \sqrt{D_1/D_2}$. Using the values of C_1D_1 and C_2D_2 in pairs, we calculated the molar extinction coefficients for the four wavelengths: $\epsilon_{540} = 1050 \pm 180$; $\epsilon_{530} = 1850 \pm 270$; $\epsilon_{520} = 3030 \pm 320$ and $\epsilon_{510} = 3560 \pm 475$. The accuracy of the values of ϵ was established by the methods outlined in [19].

Knowing ϵ, and using the results given in Table 1, the authors calculated by means of the formula for Beer's law, the equilibrium concentrations of the complex, and then K_1. Results of these calculations are given in Table 1. $K_I = 7.5 \pm 0.5$. Since $K_I = K_1 \cdot K_2'$ and $K_1 = 8.2 \times 10^{-7}$, $K_2' = 9.2 \times 10^6$ and the instability constant of the complex $K_2 = 1.1 \times 10^{-7}$. As we see, the complex with copper is somewhat more stable than the corresponding complex with nickel, for which $K_2 = 1.3 \times 10^{-6}$ [9].

With increasing pH, complexes with a more complex composition appear in solution. As is evident from Fig. 2, at a pH of 4, formation of a complex CuR_2 is possible, although the maximum on the "ΔD -composition" curve is poorly defined. Careful examination of the absorption curves shown in Fig. 1 show that up to pH4, the maximum is located at 480 mμ, while at pH 5 and higher it is found at 490 mμ. All these facts indicate that if formation of an intermediate complex CuR_2 were possible, then its concentration should be very low. A similar state of affairs was observed for the nickel complexes. Assuming that in the given case also it is possible, to a first approximation, to neglect formation of a complex CuR_2, we studied the equilibrium at pH 6 and 7, where one might expect mainly formation of the complex CuR_3^- according to the reaction

$$CuR^+ + 2RH \rightleftharpoons CuR_3^- + 2H^+ \quad (6)$$

for which

$$K = \frac{[CuR_3^-][H^+]^2}{[CuR^+][RH]^2} \quad (7)$$

First, using the saturation method, we found the molar extinction coefficients for the complex CuR_3^-. For this mixtures were made up which contained excess nitroso-N-salt as compared with the copper ions, while the pH was adjusted to 7. Having measured the optical density of the solutions, and taking into account the intrinsic color of the nitroso-N-salt, the molar extinction coefficients were calculated by means of Beer's formula; these are given in the form of absorption curves in Fig. 3. At 540, 530 and 520 mμ they were found to be respectively: 4610, 6930, and 9500. Afterwards, measurements were made of the optical density of solutions with concentrations of $C_{Cu^{2+}} = 2.0 \times 10^{-4}$ and $C_{RH} = 6.0 \times 10^{-4}$ M/liter at pH 6.0 and 7.0 and at 540, 530, and 520 mμ.

Assuming that equilibrium (6) holds good, it is possible to write

$$D = \epsilon_{CuR}[CuR^+] + \epsilon_{CuR_3}[CuR_3^-] \quad (8)$$

$$C_{Cu^{2+}} = [CuR^+] + [CuR_3^-] \quad (9)$$

Simultaneous solution of these equations gives

$$[CuR_3^-] = \frac{D - \epsilon_{CuR} \cdot C_{Cu^{2+}}}{\epsilon_{CuR_3} - \epsilon_{CuR}} \quad (10)$$

Calculating the value of $[CuR_3^-]$ by means of (10), it is then possible to find the remaining equilibrium concentrations, and, finally K. Table 2 contains the results of these calculations: $K = (5.2 \pm 2.6) \times 10^{-3}$.

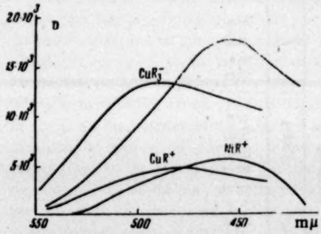

Fig. 3. Absorption curves for complexes of nitroso-N-salt with nickel and copper ions.

The sum of equations (3) and (6) gives

$$Cu^{2+} + 3RH \rightleftharpoons CuR_3^- + 3H^+ \quad (11)$$

for which $K_{II} = K_I \cdot K = 3.9 \times 10^{-2}$. On the other hand, $K_{II} = K_I^3 K_3'$, where K_3' is the constant for formation of the complex according to the equation

$$Cu^{2+} + 3R^- \rightleftharpoons CuR_3^-. \quad (12)$$

Consequently, the instability constant $K_3 = 1.4 \times 10^{-17}$. As we can see the complex CuR_3^-, just like CuR^+, is more stable then the corresponding nickel complex [9].

In conclusion, measurements were made of the optical densities of solutions in the pH range 2-5. The composition of the solutions was the same as in the previous experiments. If one disregards the formation of CuR_2, then in the pH range 2-5 we can confine ourselves to a consideration of the following equilibria:

$$Cu^{2+} + RH \rightleftharpoons CuR^+ + H^+ \quad (3)$$

$$CuR^+ + 2RH \rightleftharpoons CuR_3^- + 2H^+ \quad (6)$$

Here, $[Cu^{2+}]$, $[RH]$, $[CuR^+]$, and $[CuR_3^-]$ are not known; while $[H^+] = h$, K_I and K, and also $C_{Cu^{2+}} = 2.0 \times 10^{-4}$ and $C_{RH} = 6.0 \times 10^{-4}$ M are known.

TABLE 1

Measured Optical Densities (D) of Solutions and Calculations of the Equilibrium Constant K_I. $C_{Cu} = C_{RH}$; pH = 2,15; l = 2 cm; t° = 20°

C_{Cu} Mol/liter	λ=540 mμ			λ=530 mμ			λ=520 mμ			λ=510 mμ		
	D	$[\mathrm{CuR}^+]$	K_I	D	$[\mathrm{CuR}^+]$	K_I	D	$[\mathrm{CuR}^+]$	K_I	D	$[\mathrm{CuR}^+]$	K_I
$1{,}2 \cdot 10^{-3}$	1,12	$5{,}3 \cdot 10^{-4}$	8,5	1,98	$5{,}3 \cdot 10^{-4}$	8,5	3,16	$5{,}2 \cdot 10^{-4}$	8,0	3,77	$5{,}3 \cdot 10^{-4}$	8,4
$1{,}0 \cdot 10^{-3}$	0,83	$3{,}9 \cdot 10^{-4}$	7,7	1,26	$3{,}4 \cdot 10^{-4}$	5,6	2,17	$3{,}6 \cdot 10^{-4}$	6,1	2,46	$3{,}5 \cdot 10^{-4}$	5,7
$6.0 \cdot 10^{-4}$	0,43	$2{,}1 \cdot 10^{-4}$	9,3	0,70	$1{,}9 \cdot 10^{-4}$	7,9	1,06	$1{,}7 \cdot 10^{-4}$	6,9	1,28	$1{,}8 \cdot 10^{-4}$	7,2
$4.0 \cdot 10^{-4}$	0,21	$1{,}0 \cdot 10^{-4}$	7,9	0,38	$1{,}0 \cdot 10^{-4}$	8,2	0,57	$9{,}4 \cdot 10^{-5}$	7,1	0,64	$9{,}4 \cdot 10^{-5}$	7,1
$3{,}0 \cdot 10^{-4}$	0,15	$7{,}1 \cdot 10^{-5}$	9,6	0,23	$6{,}2 \cdot 10^{-5}$	7,8	0,34	$5{,}6 \cdot 10^{-5}$	6,7	0,40	$5{,}6 \cdot 10^{-5}$	6,7

TABLE 2

Calculated Equilibrium Constant K $C_{Cu} = 2.0 \times 10^{-4}$ M/liter; $C_{RH} = 6.0 \times 10^{-4}$ M/liter; l = 1 cm

pH	λ=540 mμ				λ=530 mμ				λ=520mμ			
	D	$[\mathrm{CuR}_2^-]$	$[\mathrm{CuR}^+]$	K	D	$[\mathrm{CuR}_2^-]$	$[\mathrm{CuR}^+]$	K	D	$[\mathrm{CuR}_2^-]$	$[\mathrm{CuR}^+]$	K
6,00	0,85	$1{,}80 \cdot 10^{-4}$	$2{,}0 \cdot 10^{-5}$	$5{,}6 \cdot 10^{-3}$	1,30	$1{,}83 \cdot 10^{-4}$	$1{,}7 \cdot 10^{-5}$	$9{,}4 \cdot 10^{-3}$	1,75	$1{,}76 \cdot 10^{-4}$	$2{,}4 \cdot 10^{-5}$	$3{,}2 \cdot 10^{-3}$
7,00	0,91	$1{,}96 \cdot 10^{-4}$	$4{,}0 \cdot 10^{-6}$	$7{,}7 \cdot 10^{-3}$	1,32	$1{,}95 \cdot 10^{-4}$	$5{,}0 \cdot 10^{-6}$	$3{,}9 \cdot 10^{-3}$	1,86	$1{,}93 \cdot 10^{-4}$	$7{,}0 \cdot 10^{-6}$	$1{,}4 \cdot 10^{-3}$

In a previous communication [9] we derived equation (17), by means of which a similar system of equilibria was calculated. In the given instance the equation has the form

$$\frac{KK_1}{h^3}[\mathrm{RH}]^4 + \frac{K_1}{h}[\mathrm{RH}]^2 + \left(1 + \frac{K_1 \cdot C_{\mathrm{Cu}^{2+}}}{h} - \frac{K_1 \cdot C_{\mathrm{RH}}}{h}\right)[\mathrm{RH}] - C_{\mathrm{RH}} = 0. \qquad (13)$$

By means of this equation we determined [RH], and then $[\mathrm{CuR}^+]$ and $[\mathrm{CuR}_3^-]$ for each pH value, i. e., we determined the concentrations of the colored components of the equilibria at 540, 530, and 520 mμ. Knowing these concentrations and the molar extinction coefficients of complexes CuR^+ and CuR_3^-, the optical densities of the solution were calculated. Results of these calculations are given in Table 3. As is evident from this table, the measured values of the optical density (D_{measured}) are in good agreement with the calculated values ($D_{\mathrm{calculated}}$) at all the pH values. This indicates that only the complexes CuR^+ and CuR_3^- are really mainly found in solution, while if any CuR_2 is formed, its concentration lies within the limits of experimental error.

TABLE 3

Calculated Equilibrium Concentrations as Functions of the pH

pH	[RH]	$[\mathrm{Cu}^{2+}]$	$[\mathrm{CuR}^+]$	$[\mathrm{CuR}_3^-]$	D_{540}		D_{530}		D_{520}	
					calc.	meas.	calc.	meas.	calc.	meas.
2,55	$4,8\cdot10^{-4}$	$8,7\cdot10^{-5}$	$1,1\cdot10^{-4}$	$1,5\cdot10^{-9}$	0,12	0,12	0,21	0,18	0,34	0,27
2,95	$4,5\cdot10^{-4}$	$5,0\cdot10^{-5}$	$1,5\cdot10^{-4}$	$1,1\cdot10^{-8}$	0,16	0,16	0,28	0,25	0,45	0,43
3,50	$4,2\cdot10^{-4}$	$1,8\cdot10^{-6}$	$1,8\cdot10^{-4}$	$1.4\cdot10^{-7}$	0,19	0,16	0,34	0,32	0,57	0,60
4,00	$3,8\cdot10^{-4}$	$6,4\cdot10^{-6}$	$1,8\cdot10^{-4}$	$1,2\cdot10^{-5}$	0,24	0,21	0,44	0,49	0,68	0,72
5,00	$1,5\cdot10^{-4}$	$9,3\cdot10^{-7}$	$1,0\cdot10^{-4}$	$9,7\cdot10^{-5}$	0,56	0,60	0,86	0,90	1,23	1,25

In Fig. 3 are shown the absorption curves for the complexes formed between nitroso-N-salt and nickel and copper. The complexes NiR_3^- and CuR_3^- are important from an analytical point of view, since their absorption curves differ to such an extent, that, presumably, it should be possible to carry out a spectrophotometric determination of copper and nickel ions when they are present together.

As noted above, the complex CuR_3^- is more stable than the complex NiR_3^-; this is in agreement with the well-known fact that copper complexes are more stable than nickel complexes [20]. As for the spectral characteristics, the results obtained do not agree with the assumption that the absorption curves for the more stable complexes (similar in structure) should be displaced to a greater extent towards the short-wave side than the absorption curves for the less stable complexes [21]. Apparently, there is no such simple relationship here. Difficulties arise in trying to explain the nature of complexes. The complex CuR^+, obviously, is of the intercomplex type of compound, in which all the valence of the copper is not saturated. As for the complex CuR_3^-, then taking into account the divalence of copper, this complex is best related to the acidocomplex type. As can be seen from the absorption curves (Fig. 3), the maximum on the absorption curve for the complex CuR^+ is insignificantly displaced towards the red side (by 10-15 mμ) on connecting another two molecules of RH to CuR^+. This indicates that the bond between these two molecules in the complex CuR_3^- is electrostatic in character. In this case the spectra have an approximately additive character. The small shift of the absorption toward the red side is caused by the intermolecular Stark effect as a result of the field of the connected molecules of the nitroso-N-salt distorting the system of terms of the CuR^+ complex [22].

The authors wish to thank N. P. Komar' for his continued interest in the work.

SUMMARY

It has been established that two complex ions, CuR^+ and CuR_3^-, are formed in solutions containing copper ions and sodium 2-nitroso-1-naphthol-4-sulfonate, depending on the pH of the solution. The molar extinction coefficients of these complexes have been calculated as well as their instability constants. The complexes with copper ions are more stable than the corresponding complexes with nickel ions.

The NiR_3^- and CuR_3^- complexes are fairly stable and have high molar extinction coefficients. The difference in their absorption curves is large enough to permit the spectrophotometric determination of copper and nickel ions when present together.

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PRECIPITATION CHROMATOGRAPHY ON PAPER AS A METHOD FOR DETERMINING THE RELATIVE SOLUBILITY OF SPARINGLY SOLUBLE COMPOUNDS

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Studies carried out in order to elucidate the effect of various factors on the development of the zones of precipitates of individual sparingly soluble compounds led to the conclusion that the final dimensions of the zone belonging to one precipitate or another on the washed chromatogram is determined by the following factors: 1) by the value of the solubility product of the sparingly soluble precipitate (linear relationship); 2) by the concentration of the original solution (linear relationship); 3) by the volume of the drop of test solution (linear relationship); 4) by the nature of the precipitate formed (formation of crystalline precipitates terminates on a narrower part).

All other conditions being equal, the zone width of any particular precipitate on a washed chromatogram depends exclusively on the value of the solubility product of the sparingly soluble compound.

The precipitate on the washed chromatogram occupies a smaller area, the lower the value of its solubility product, and consequently the lower its solubility. Obviously, it should therefore be possible to assess the relative solubility of various precipitates on the basis of the zone width of these precipitates on a washed chromatogram.

In order to obtain data on the comparative solubility of various precipitates, it is necessary to obtain washed precipitation chromatograms of the individual sparingly soluble compounds. The washed chromatograms must be developed. On the developed chromatograms it is then necessary to determine the zone dimensions of the corresponding precipitates, and the results obtained compared with each other. As a result it is possible to compile a series of precipitates in decreasing or increasing order of solubility. The least soluble precipitates form the zones with the smallest dimensions on the chromatogram.

Method and Experimental Technique

Reagent paper was prepared by soaking ordinary filter paper (OST 6717/58) with 1-4% aqueous solutions of the alkali metals which serve as the precipitant. Excess solution was allowed to drain, and the paper bands then dried in air in a hanging position.

The primary chromatogram was obtained by placing a drop of 0.1 N test solution by means of a capillary provided with a rubber bulb, on a band of reagent paper 65 x 65 mm. During this stage the drop was allowed to drop freely into the paper from a height not greater than 5 mm from the paper surface. After the drop had dispersed in the paper pores in a radial direction, the primary chromatogram was formed in the shape of a round spot.

The washed chromatogram was obtained by placing drops of distilled water in the center of the moist round spot in succession, in the same way as that adopted for obtaining the primary chromatogram. In order to get the final dimenssions of the zone it was necessary to superimpose five-six drops of water. Each new drop was placed on the paper only after the preceding drop had completely soaked in.

The washed chromatogram was also the developed chromatogram in those cases where the precipitate formed had its own intrinsic color. In those cases where precipitate was colored, it was developed by means of a reagent which reacts with it to give colored compound.

The chromatograms were developed by spraying the dry, washed chromatogram with a solution of developing reagent supplied from a sprayer. The developer was applied to the paper observing the following conditions: a) the solution was applied in a fine uniform spray; b) the solution was applied in several small portions; c) excessive soaking was avoided, a new portion only being applied after the former had been completely absorbed.

The zone of an individual sparingly soluble compound on the developed chromatogram was in the form of a colored round spot. In the case of two more precipitates applied simultaneously, the soluble precipitate formed the center in the form of a round spot, while the others formed colored rings surrounding the center spot. The precipitates follow one another from the center to the periphery in order of increasing solubility.

Test Materials and Experimental Results

The relative solubility of silicates, phosphates, arsenites, ferrocyanides, chromates, and several other sparingly soluble compounds was determined by precipitation chromatography on paper by the drop variant. In order to get the precipitation chromatograms, the paper was treated with the following solutions of the alkali metal salts respectively: 4% sodium silicate, 3.5% sodium hydrogen phosphate (disubstituted), 3.5% sodium arsenite, 1.0% potassium ferrocyanide, and 3% potassium chromate. The paper soaked with potassium ferrocyanide contained the equivalent amount of precipitant with respect to the test ions. Bearing in mind that complex formation proceeds stepwise, with formation of coordinately saturated and unsaturated compounds [1], and also of mixed compounds [2], other concentrations of the precipitant (0.5-5%) were tried in addition to those mentioned above. The content of other precipitants in the reagent paper was two-three times the equivalent amount of the test ions.

Calculation of the concentrations of the solutions to be used for treating the paper, so that the paper contained the equivalent amount of precipitant in the zone where formation of the given precipitate occurs, was based on the following. When a volume V (cm^3) of test solution in the form of drop flows along the pores of the paper, and its concentration is Co(mg-equivalent / cc) the absorption capacity of the precipitant should be given by;

$$A = Sh\gamma a,$$

where S is the in cm^2 area of the paper, on which the drops of test solution (cc) spread; h is the paper thickness in cm; γ is the density of the precipitant in the paper pores, in mg/cm^3; and α is the specific absorption capacity of the precipitant, in mg-equivalents/ mg.

In accordance with the law of equivalents and with the law of conservation of matter, the following equation should hold:

$$Sh\gamma a = CoV. \tag{1}$$

The product $Sh\gamma$ is the weight (g) of precipitant in the volume in which formation of precipitate occurs, while the reciprocal of the specific absorption capacity of the precipitant (1/ a) is simply its equivalent weight (E). Taking this into account, relation (1) can be expressed as

$$g = CoV \cdot E. \tag{2}$$

The weight of precipitant (g) corresponding to the volume of the drop of test solution is expressed in mg. In order to convert its concentration into grams per 100 ml of solution (G) the following formula is suitable:

$$G = Co \cdot E \cdot 100. \tag{3}$$

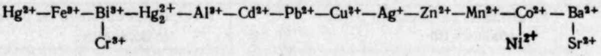
The materials to be precipitated were used in the form of 0.1 N solutions of the nitrates of those cations which form sparingly soluble compounds with a given precipitant. The drop volume of the solutions prepared was measured with a microburet (the volume was 0.025 ml). In all experiments the concentrations of the solutions of the materials being precipitated, and also the volume of the drops were kept constant. Under these conditions, the difference in the dimensions of the zones of the precipitates obtained could only be attributed to the differences in the solubilities of the precipitates.

The developers used (Table 1) were organic reagents which formed with the precipitates on the washed chromatogram, even less soluble compounds with a bright characteristic color. The zone width of the precipitates of individual sparingly soluble compounds were measured on the developed chromatograms with an accuracy of 0.1 mm. The results obtained are given in Table 2.

When the precipitates differed from each other with respect to solubility, the zone dimensions of the separate precipitates on paper soaked with the same precipitant, differed from each other. From the relative dimensions of the zone of the precipitates studied, a scale was compiled of the comparative solubilities of these precipitates on the basis of the linear relationship between the width of the precipitate zone on the developed chromatogram and its solubility.

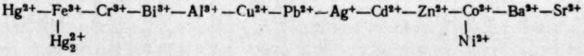
In order to fix the position of each member in a sorption series of solubility more accurately, the elements were taken in pairs. When the pair of cations taken separated in the form of precipitates, two zones were found on the developed chromatogram. The first zone, belonging to the least soluble of the two precipitates, was obtained in the form of a round spot with a characteristic color, in the center, at the point where the drop of test solution was placed on the paper. The zone of the more soluble precipitate was located on the periphery of the first zone in the form of a ring of a different color. Precipitates which were equally soluble appeared as a mixed zone on the developed chromatogram. In the sorption series of solubility such precipitates occupy the same position. The following series of precipitate solubilities were obtained (the series are in increasing order of solubility):

1. The series obtained on a paper soaked with sodium silicate



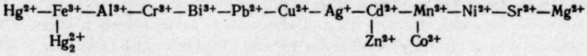
$$\mathrm{Hg^{2+}—Fe^{3+}—}\underset{\underset{\mathrm{Cr^{3+}}}{|}}{\mathrm{Bi^{3+}}}\mathrm{—Hg_2^{2+}—Al^{3+}—Cd^{2+}—Pb^{2+}—Cu^{2+}—Ag^{+}—Zn^{2+}—Mn^{2+}—}\underset{\underset{\mathrm{Ni^{2+}}}{|}}{\mathrm{Co^{2+}}}\mathrm{—}\underset{\underset{\mathrm{Sr^{2+}}}{|}}{\mathrm{Ba^{2+}}}$$

2. The series obtained on paper soaked with sodium arsenite



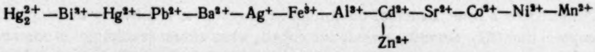
$$\mathrm{Hg^{2+}—}\underset{\underset{\mathrm{Hg_2^{2+}}}{|}}{\mathrm{Fe^{3+}}}\mathrm{—Cr^{3+}—Bi^{3+}—Al^{3+}—Cu^{2+}—Pb^{2+}—Ag^{+}—Cd^{2+}—Zn^{2+}—}\underset{\underset{\mathrm{Ni^{2+}}}{|}}{\mathrm{Co^{2+}}}\mathrm{—Ba^{2+}—Sr^{2+}}$$

3. The series obtained on paper treated with sodium hydrogen phosphate (disubstituted)



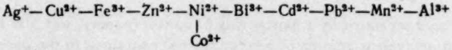
$$\mathrm{Hg^{2+}—}\underset{\underset{\mathrm{Hg_2^{2+}}}{|}}{\mathrm{Fe^{3+}}}\mathrm{—Al^{3+}—Cr^{3+}—Bi^{3+}—Pb^{2+}—Cu^{2+}—Ag^{+}—}\underset{\underset{\mathrm{Zn^{2+}}}{|}}{\mathrm{Cd^{2+}}}\mathrm{—}\underset{\underset{\mathrm{Co^{2+}}}{|}}{\mathrm{Mn^{2+}}}\mathrm{—Ni^{2+}—Sr^{2+}—Mg^{2+}}$$

4. The series obtained on paper soaked with potassium chromate



$$\mathrm{Hg_2^{2+}—Bi^{3+}—Hg^{2+}—Pb^{2+}—Ba^{2+}—Ag^{+}—Fe^{3+}—Al^{3+}—}\underset{\underset{\mathrm{Zn^{2+}}}{|}}{\mathrm{Cd^{2+}}}\mathrm{—Sr^{2+}—Co^{2+}—Ni^{2+}—Mn^{2+}}$$

5. The series obtained on paper soaked with potassium ferrocyanide



$$\mathrm{Ag^{+}—Cu^{2+}—Fe^{3+}—Zn^{2+}—}\underset{\underset{\mathrm{Co^{2+}}}{|}}{\mathrm{Ni^{2+}}}\mathrm{—Bi^{3+}—Cd^{2+}—Pb^{2+}—Mn^{2+}—Al^{3+}}$$

The solubility series obtained for the ferrocyanides differs from the series obtained previously [3].

The reason for the difference in the experimental results is that the composition and the properties (including solubility) of the ferrocyanides depend on the conditions used for preparing them. As indicated already [2], in addition to simple ferrocyanides of the type $\mathrm{Me_2^{2+}[Fe(CN)_6]}$, there may also be formed mixed (binary and ternary) salts.

By a series of experiments it was established that the relative dimensions of the zones of the ferrocyanide precipitates of different metals, as well as their differentiation during separation of pairs of metals, depend significantly on the concentration of the precipitant in the paper. Copper and iron (III), cobalt and zinc, and

TABLE 1

Reagents-Developers

Developer	Concen., g/100 ml of solution	Solvent	Cations whose precipitate zones are developed
Alizarin —$C_{14}H_8O_4$	0,1	Alcohol	Al^{3+}, Fe^{3+}
Aluminon —$C_{22}H_{23}O_9N_3$	0,1	Distilled water	Al^{3+}, Cr^{3+}, Fe^{3+}
Benzidine–$C_{12}H_{12}N_2$	0,1	Acetic acid (50%-solution)	Mn^{2+}
Dithiozone–$C_{13}H_{12}N_4S$	0,05	Benzene	Zn^{2+}, Ni^{2+}, Co^{2+}, Ag^+, Hg_2^{2+}, Hg^{2+}, Cu^{2+}, Ca^{2+}
Magneson–$C_{12}H_9O_4N_3$	0,025	Na OH (0,1 *N* solution)	Mg^{2+}
Sodium rhodizonate $C_6H_6Na_2$	0,1	Distilled water	Ba^{2+}, Sr^{2+}, Pb^{2+}
Rubeanic acid —$C_2H_4N_2S_2$	0,2	Alcohol	Ni^{2+}, Co^{2+}, Cu^{2+}

TABLE 2

Dimensions of the Zones of Various Precipitates (in mm)

Cations	Precipitates obtained on paper soaked with:					Cations	Precipitates obtained on paper soaked with:				
	Na_2SiO_3	Na_2HPO_4	Na_3AsO_3	$K_4[Fe(CN)_6]$	K_2CrO_4		Na_2SiO_3	Na_2HPO_4	Na_3AsO_3	$K_4[Fe(CN)_6]$	K_2CrO_4
Mg^{2+}	—	38,16	—	—	—	Co^{2+}	24,8	29,5	21,6	27,5	49,0
Sr^{2+}	25,8	36,0	27,2	—	42,5	Ag^+	21,5	27,5	16,3	14,5[31]	19,6
Ba^{2+}	25,7	29,3	25,0	—	22,2	Hg^{2+}_2	14,0	11.0	11,1	—	9,4
Al^{3+}	14,8	14,6	15.0	44,5	29,0	Pb^{2+}	16,8	18,0	16.1	30,5	17,4
Cr^{3+}	13,2	14,0	11,9	—	—	Hg^{2+}	7,8	8,0	9,6	—	11,2
Fe^{3+}	10,4	11,2	11,1	23,5	23,2	Bi^{3+}	13,2	17,6	12,7	28 5	10,0
Mn^{2+}	24,1	29,3	—	40,0	50,0	Cu^{2+}	20,0	22,5	15,6	22,0	36,1
Zn^{2+}	23,0	28.0	21,0	25,5	39,0	Cd^{2+}	16,0	28,0	20,0	30,0	39,0
Ni^{2+}	24,9	32,8	21,6	27,7	47,0						

also nickel and zinc, were not separated on paper soaked with 5% potassium ferrocyanide solution (excess precipitant), but were separated on paper soaked with 1% potassium ferrocyanide solution (an equivalent amount of precipitant). This could be a consequence of the formation of compounds differing in composition and solubility. Precipitates of copper, iron (III), bismuth, nickel, and cobalt, when excess precipitant is contained in the paper, separate out in the center (as a spot) and on the periphery (as a ring). When excess precipitant is used, presumably, there is obtained mixed (binary), appreciably soluble compounds which at the extreme position of the spot, after washing the primary chromatogram, are precipitated again.

Formation of two zones separated by a narrow ring of carrier (paper), was also observed in the case of silver precipitates when an equivalent amount of precipitate was contained in the paper. They were visible only at the moment of development (with dithizone). During separation of silver and copper in pairs these precipitates of silver which differ in properties and solubility were separated by the copper zone. It is an interesting fact with time these precipitates migrated; the more soluble silver zone migrated to the center, while the copper zone shifted towards the periphery of the spot.

Zinc and cadmium on separate chromatograms formed precipitates; the relative dimensions of zones indicated the possibility of separating these metals when taken in pairs. Nevertheless, when an attempt was made to separate these metals a mixed zone was obtained, this being presumably a consequence of the formation of binary and perhaps ternary salts.

It should be pointed out that the precipitates obtained on paper impregnated with other precipitants, sometimes differed in their composition from the composition of the corresponding salts. On paper impregnated with sodium silicate, iron ions (III) gave a precipitate of hydrated oxide with a cinnamon-brown color and not iron silicate, as a result of hydrolytic decomposition of the latter. On paper impregnated with sodium arsenite, cations of aluminum, chromium, and iron (III) formed hydroxide precipitates while bismuth gave precipitates of basic salts. The remaining cations gave arsenite precipitates. Hydroxide precipitates of aluminum, chromium, and i iron (III) (instead of phosphates) were formed on paper impregnated with sodium hydrophosphate. Bismuth separated out as the phosphate on the chromatogram.

The practical importance of a solubility series lies in the fact that they can furnish a basis for a possible separation of complex mixtures of materials. The members of any particular solubility series are more completely separated from one another, the further removed they are from each other in the series. Another criterion for completeness of separation of a mixture of materials in the form of precipitates, is the coefficient for the mean relative rate of movement of the precipitates K_b [3] which is defined by the equation

$$K_b = \frac{d_{M+A^-}}{d_{K+A^-}} = \frac{pL_{K+A^-}}{pL_{M+A^-}} \ldots, (1)$$

where d_{M+A^-} and d_{K+A^-} are the diameters of the zones of the precipitates of the least soluble and most soluble compound, respectively, while pL_{M+A^-} and pL_{K+A^-} are the indices of the solubility products of these compounds.

It was established that a pair of inorganic ions can be completely separated in the form of precipitates on paper, when the value of K_b is equal to and less than 0.75. Partial separation of the precipitates of various metals is possible even for higher values of K_b, starting at a value of 0.95-0.96. Under these conditions, the smaller the value of K_b the more complete their separation. K_b can be said to be a quantitative measure of completeness of separation. K_b can be established merely by measuring the areas of the zones of the precipitates under consideration on the developed chromatograms and taking the ratio of the smaller area to the larger area. If it should prove to be less than 0.75, then complete separation of the precipitates should be possible.

Determination of the comparative solubility of precipitates by means of the method of precipitation chromatography on paper has not been studied in detail. The method enables one to get preliminary results to help in choosing the method of precipitation to be used for the separation of a complex mixture of materials.

SUMMARY

The possibility has been demonstrated of using precipitation chromatography on paper in a drop variant as a simple and rapid method of determining the relative solubility of sparingly soluble compounds. Sorption series for the comparative solubility of the silicates, arsenites, phosphates, chromates, and ferrocyanides of a large number of metals have been obtained.

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DETERMINATION OF THE ALKALI AND ALKALINE EARTH ELEMENTS IN SILICATE ROCKS BY MEANS OF FLAME SPECTROPHOTOMETRY

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Determination of the alkali and alkaline-earth elements in rocks is the most difficult operation in chemical analysis. For speeding up the determination of sodium and potassium in silicate rocks, Osborn [1] first used the method of flame photometry. Brannock and Berthold [2] used this method later for the analysis of minerals. The problem of the other alkali and alkaline-earth elements has been considered by other authors [3-9], but in each of these cases only one or two of the elements were considered, and only Horstman [10] determined rubidium, and cesium in the same solution. It is often necessary, however, for geochemical purposes, to determine the content of all the alkali and alkaline-earth elements in rocks and minerals simultaneously.

The work described in the present article is devoted to the development of a method for determining the alkali and alkaline-earth elements in granites, gneiss, syenites, microcline, and other silicate rocks and minerals. The spectrophotometer constructed is suitable for the determination of the alkali and alkaline-earth elements in an air-acetylene flame.

The optical system was a "DM" double-glass monochromator. The photoelectric setup includes a FÉU-17 photomultiplier (for the visible part of the spectrum) and a FÉU-22 photomultiplier (for the red and infrared part of the spectrum), a VVS-1 rectifier, and a M-21 mirror galvanometer with a sensitivity of 1×10^{-9} amp /mm. A spherical mirror 10 cm in diameter was set up behind the burner; this increased the sensitivity of the apparatus almost twice. The width for the inlet and outlet slits were chosen in the limits 0.05-0.08 mm for strontium and rubidium, while for sodium, potassium, lithium, and calcium this width was 0.08-0.12 mm. When lithium was determined in the presence of considerable amounts of strontium and calcium, the slit width was decreased to 0.05 mm and aluminum was added to the solution until its concentration was 1.5 mg/ml for decreasing the intensity of the strontium and calcium lines in the 670 mμ region. The indicated slit widths were the optimum values, since on increasing the slit width, the background increased more rapidly than the line intensity. By using a photomultiplier of a sufficiently high quality it was found possible to attain a sensitivity, in terms of γ/ ml, of 0.005 with respect to lithium, 0.003 for sodium, 0.005 for potassium, 0.01 for rubidium, 0.05 for calcium, and 0.05 for strontium, when pure salts were used (for a deflection of the galvanometer through one division). Measurements of the emission intensity were carried out on the basis of the following lines: lithium 670.8 , potassium 766.5 , sodium 588.9, rubidium 780.0 or 794.7 , calcium 549.8, strontium 460.7 mμ. The background was measured on both sides of the lines and the mean value taken.

During determination of group I and II elements, the test material was treated with hydrofluoric acid and perchloric acids. Other methods of decomposing test material were inapplicable; when sulfuric acid was used precipitates of the sulfates of the second group were formed, while on fusing test material with potassium or sodium carbonates, it is no longer possible to determine these elements.

A necessary condition for the determination of calcium and strontium is the absence of aluminum, which depresses the emission as a result of the formation of chemical compounds with high melting points.

TABLE 1

Activ. of the added Sr, impulses/min	Extraction with:	Activ. of the Sr extracted, impulses/min	Sr extracted, %
9380	H_2O	6715	71,4
9380	H_2O	8260	88,1
9380	2*N* HCl	9312	99,3
9380	2*N* HCl	9400	100

Removal of aluminum as the hydroxide can lead to adsorption of the alkali and alkaline-earth elements, so that reprecipitation is necessary. In order to avoid this we adopted Ahrens' method of concentrating the alkali and alkaline-earth elements [11], this consists in calcining the dry perchlorates and subsequently extracting the alkali and alkaline-earth elements with water. For this purpose we used 2 N HCl, completeness ofextraction was controlled by using radioactive strontium Sr^{90} . The results obtained are given in Table 1.

EXPERIMENTAL PROCEDURE

An aliquot of carefully ground silicate (0.7-1.0 g) contained in a platinum basin is moistened with a few drops of water and 5-10 ml of perchloric acid and 15-20 ml of hydrofluoric acid added. The mixture is evaporated until the appearance of perchloric acid fumes. If the rock should not be completely decomposed after the first evaporation, the process is repeated with 5-10 ml of HF. For complete removal of fluoride after decomposition of the rock, the mixture is evaporated twice almost to dryness, a few drops of water and perchloric acid being added each time. The dry residue of perchlorates is then calcined at 500-550° for one hour. The perchlorates of the alkali metals are thereupon converted into the chlorides, while the alkaline-earth perchlorates are converted into the chlorides and partly into the oxides, and the perchlorates of the other elements into their oxides. The calcined residues are heated twice with 50 ml of 2 N hydrochloric acid ,then twice with water, the solutions being collected each time in a beaker. During these operations only an insignificant part (5-7%) of the aluminum and iron oxides dissolve . Aluminum and iron are removed from the solution thus obtained by precipitation with ammonia (1:1) free from carbonate, the solution being neutralized to the methyl red endpoint. The precipitate is filtered off and washed; the solution is evaporated and then transferred to a 50 ml standard flask. For the determination of potassium and sodium, the content of which in rocks is rarely less than 1%, an aliquot of the solution is diluted so that the final concentration of potassium and sodium is within the range 5 to 50 γ/ml. The solution is always diluted when the content of the element to be determined is higher than the concentration at which there is observed a linear relation between concentration and emission. These concentrations, for which a linear relation is observed, were found to be up to 30 γ/ ml. for lithium, up to 50-70 γ/ml for sodium, potassium, and rubidium, and up to 100-120 γ/ml for calcium and strontium.

The effect of various cations and anions on the emission of the alkali and alkaline-earth elements has been studied in detail in a number of paper [5, 12-14]. The choice of standards for test materials with an average content (more than 0.01%) of the alkali and alkaline-earth elements does not present any particular difficulty. For determination of lithium, rubidium, and strontium in granites, gneiss, and syenites, the standards contain potassium, sodium, calcium, and magnesium. To the standards for determining these elements, 1 ml of a solution containing 5% K_2O, 5.5% NaO, 0.5% CaO, and 0.5% MgO is added. For the analysis of rocks with a higher content of CaO and MgO, the amount of these elements added is increased to 2%. During determination of one of the three elements Na, K, and Ca, the standards used contain the other two elements in amounts equivalent to their content in the test rocks. Thus, for determination of potassium, the standards contain sodium and calcium. When the contents of the alkali and alkaline-earth elements is lower than 0.01%, the method of additions is used [15], in which the test solution is also the standard solution. For this purpose 4 aliquots of 10 ml each are taken from the original solution and transferred to 25-ml flasks. Water is added to one of these, while to the other three flasks are added accurate amounts of the solutions of the salts, so that the first of these flasks contains approximately the same amount of added salt as there is in the test material, while the second and third flasks contain twice , and four times the amount of added salt as there is in the first flask (see Table 2). The solutions obtained are then measured flame-photometrically, the background being measured on both sides of the lines. The background value is subtracted from the intensity of the line and the results plotted graphically (Fig. 1). The curve obtained is linear as long as the highest concentration of the salt does not exceed the values indicated above. The segment on the abscissa from the point of intersection of the straight line to the origin gives the content of the test elements in solution.

In order to check the method of additions, several experiments were carried out with synthetic mixtures to which various amounts of sodium, potassium, barium, and various acids were added. As the results in Table 3 show the error rarely exceeds limits of 5%. For low contents of several of the alkali and alkaline-earth elements

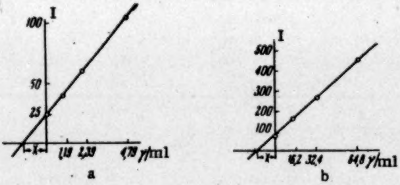
TABLE 2

Taken, γ /ml		Added, γ / ml						Found, γ / ml		Error	
		Flask 1		Flask 2		Flask 3					
Sr^{++}	Ca	Sr	Ca	Sr	Ca	Sr	Ca	Sr	Ca	Sr	Ca
1,33	15,6	1,19	16,2	2,39	32,4	4,79	64,8	1,36	15,4	+2,2	—1,3
26	82	48	171	68	266	113	449	Galvanometer deflection, background taken into account			

(of the order of 0.001%), the aliquot taken is increased to 1-1,5g, while 25% by volume of alcohol is added to the solution which is to be photometrically measured in order to decrease the depression of the line intensities of the alkali metals caused by the presence of a large excess of foreign salts.

The method was checked on international standard granite G-1 and diabase W-1. The results are given in Table 4.

During the determination of the alkali and alkaline-earth elements in several samples of granites, gneiss, syenites, microcline, and mica, the results given in Table 5 were obtained. The results obtained by the comparison method and by the method of additions are in good agreement with each other, and with those obtained by chemical and spectrographic methods.



Determination of the concentration of an element in solution by the method of additions: a) for Sr; b) for Ca.

TABLE 5

Rock	Method of determination	Li, %	Na, %	K, %	Rb, %	Ca, %	Sr, %
Gneiss	Comparison	—	2,20	3,77	0,0077	0,125	0,0175
	Additions	—	2,22	3,84	0,0074	0,130	0,0180
	Others	—	—	—	0,007 (s)	0,131 (c)	0,020 (s)
Gneiss	Comparison	—	2,57	3,52	0,0065	0,290	0,0084
	Additions	—	2,64	3,50	0,0070	0,280	0,0075
	Others	—	—	—	0,0070(s)	0,293(c)	0,0065 (s)
Granite	Comparison	0,0013	3,90	4,10	0,012	1 80	0,0120
	Additions	0,0014	3,80	4,00	0,011	1,80	0,0120
	Others	0,0010(s)	—	4,0	—	1,75 (c)	0,0130 (s)
Syenite	Comparison	0,0019	3,75	11,9	0,150	1,90	0,164
	Additions	0,0020	3,70	12,0	0,155	1,85	0,160
	Others	0,0020(s)	4,0 (c)	12,0(c)	0,17 (s)	2,00 (c)	—
Microcline	Comparison	0,0007	—	11,2	0,28	—	0,0022
	Additions	0,0007	—	11,3	0,29	—	0,0022
	Others	0,0009(s)	—	—	0,28 (s)	—	—

Notes: s) spectrographic method; c) chemical method.

TABLE 3

Taken γ/ml				Impurities, mg/ml			Found, γ/ml				Error, %			
Li	Rb	Sr	Ca	Na	K	Ba	Li	Rb	Sr	Ca	Li	Rb	Sr	Ca
0,80	1,50	1,33	15,6	0,3	0,4	0,2	0,85	1,55	1,36	15,4	+6,3	+3,3	+2,2	−1,3
2,40	1,50	1,33	1,56	0,3	0,4	0,2	2,30	1,55	1,29	1,51	−4,2	+3,3	−3,0	−3,2
4,80	3,00	6,65	3,12	0,5	0,4	0,3	4,80	2,90	6,51	3,2	0,0	−3,3	+2,1	+2,6
9,60	3,00	3,32	6,24	0,5	0,5	0,3	9,90	3,20	3,42	6,00	+3,1	+6,7	+3,0	−3,9
9,60	0,70	33,2	1,56	0,5	0,4	0,1	9,35	0,75	35,0	1,60	−3,0	+7,1	+5,4	+2,5
12,0	9,0	2,66	23,4	0,4	0,5	0,2	12,8	8,6	2,60	23,5	+6,4	−4,5	−2,3	+0,4
2,40	1,65	1,99	20,8	0,3	0,2	0,2	2,45	1,60	20,5	22,0	+2,1	−3,1	+3,0	+5,7
4,80	15,0	3,32	6,24	0,2	0,2	0,3	4,70	15,0	3,25	6,30	−2,1	0,0	−2,1	+1,0

TABLE 4

Rock	Method of determination	$Li\cdot10^{-4}$, %	Na, %	K, %	$Rb\cdot10^{-4}$, %	Ca, %	Sr, %
Granite G-1	Spectrographic	19; 23; 25 [16]			250 [16]		0,028 [16]
	Flame photometric	20 [10]; 24 [3]			205 [3]; 204 [10]		
	Isotopic dilution	—			215, 218 [17]		
	Neutron activation	—			221, 243, 254 [18]		
	Chemical	—	2,41 [16]	4,50 [16]	—	1,0 [16]	
	Author's results	20	2,43	4,30	202	0,97	0,029
Diabase W-1	Spectrographic	9, 9; 20 [16]			15; 20 [16]		0,029 [16]
	Flame photometric	14 [3, 10]			19; 25 [10]		
	Isotopic dilution	—			27; 29 [17]		
	Neutron activation	—			27; 29; 26; [18]		
	Chemical	—	1,50 [16]	0,53 [16]	—	7,9 [16]	—
	Author's results	9	1,57	0,54	26	8,1	0,031

SUMMARY

A method has been developed for the determination of the alkali and alkaline-earth elements in silicate rocks when the contents of these elements is not less than 0.001%.

A flame spectrophotometer with an air-acetylene burner, a monochromator, and a photomultiplier has been designed. Measurements were carried out on the basis of the following lines: Li 670.7 mμ, K 766.5 mμ, Na 588.9 mμ, Rb 780.0 mμ, Ca 549.8 mμ, and Sr 460.7 mμ.

Preliminary chemical treatment includes decomposition of the sample with hydrofluoric and perchloric acids, leaching the calcined precipitates with 2 N hydrochloric acid, and precipitating aluminum with ammonia. The experimental error does not exceed 5-6%.

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THE METHOD OF "IN SITU NASCENDI" REAGENTS

COMMUNICATION 2. THE USE OF DIOXANE DURING THE DETERMINATION OF CALCIUM AND STRONTIUM AS THEIR SULFATES*

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In our first communication [1] a description was given of the determination of the alkaline-earth metals by means of the method of "in situ nascendi" reagents using dimethyl sulfate which gradually gives SO_4^{2-} ions during hydrolysis. Separate determination of calcium and barium can be carried out by adding to the solution some glycerol, glucose, or sugar which form water-soluble, unstable complexes with the ions of the alkaline-earth metals. By adopting this technique the quality of the precipitate is improved as a consequence of the gradual appearance in solution of both SO_4^{2-}, and Ba^{2+}, and Ca^{2+} ions which arise during the dissociation of the unstable complexes with the hydroxy compounds. Willard et al [2, 3] who developed a method for precipitation in homogeneous solutions (or as we propose to call it the method of precipitation by "in situ nascendi reagents"), did not turn their attention to the significance of complexing agents, although in order to remove accompanying metals resort has often been made [4-8] to the addition of "masking" reagents. The part played by various "masking" agents, according to accepted ideas, reduces merely to the formation of more stable complexes by individual ions [2, 9-14]. We are of the opinion that the improvement in the form of the precipitation of the salt undoubtedly depends also on whether the ion to be precipitated is found in the form of a complex compound or not.

Addition of organic solvents (alcohols, acetone, etc) is usually recommended for determining the solubility of the precipitated salt. Nevertheless, in a number of cases of a similar type, reagents make it possible to prepare more suitable precipitates by forming complex compounds which are not very stable with the ion to be precipitated.

Modern organic chemistry and chemical industry have suggested many new solvents which have not yet found wide application in the practice of inorganic analysis. The present article contains some examples of the use of an active solvent of this type, namely dioxane.

Dioxane or diethylene ether $O{=}(CH_2{-}CH_2)_2{=}O$ is a liquid which boils at 101° and has a sp. gr. of 1.03; it is miscible with water and is a good solvent for organic materials. Dioxane can form unstable oxonium salts with strong acids. It forms with metal salts, mainly with halides, complex compounds which dissociate in aqueous solution ti a greater or lesser extent. Menshutkin [15, 16] as long ago as 1903 describe a number of such complexes. Thus, the halides of the alkali and alkaline-earth elements, and also some heavy metal salts form compounds —"etherates"— with dioxane. Later, a number of authors (Lynch [17], Bogardu [18], Weicksel [19], and Rheinbodt [20] et al) studied in detail the physicochemical properties of the compounds of the metal halides with dioxane.

In addition, dioxane decreases the solubility of various salts, thereby, exhibiting a salting out effect. Using these properties of dioxane, we used it in analysis of calcium and strontium. It was found that dimethylsulfate., in the presence of excess dioxane, precipitates dense, compact, fibrous precipitates of calcium and strontium sulfates from weakly hydrochloric acid or neutral solutions of calcium and strontium salts. (See fig.). The coagulation

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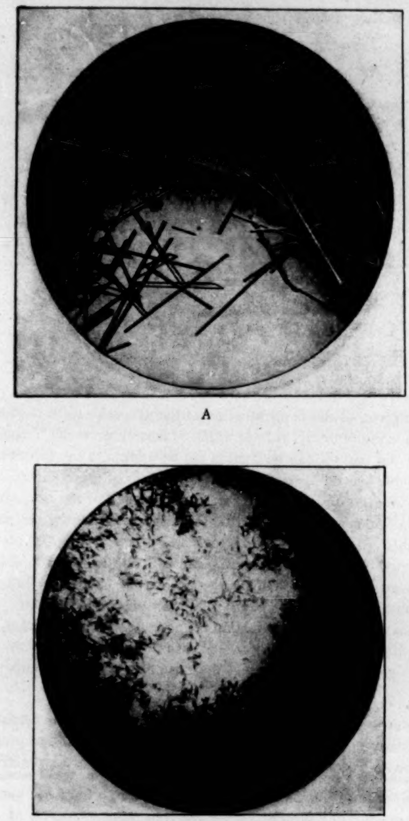
* For communication 1, see [1].



A) Calcium sulfate precipitated from an aqueous solution of calcium chloride by means of dimethyl sulfate in the presence of dioxane (× 75) ;

B) Calcium sulphate, precipitated from a 75% alcoholic solution of calcium chloride by means of sulfuric acid (× 75).

of calcium sulfate and strontium crystals is related to the fact that dioxane forms soluble complexes with calcium and strontium chlorides. When a sufficient amount of sulfate ions appear, precipitates of calcium and strontium sulfates are formed.

Precipitation of Calcium Sulfate by Means of Dimethyl Sulfate in the Presence of Dioxane

Calcium sulfate can be crystallized in the form of its dihydrate, its semihydrate, or as the anhydrous form (anhydrite).

The question of the dehydration of the crystallohydrates of calcium sulfate has occupied many authors for a long time and the results obtained are very contradictory. These results relate mainly to synthetic preparations obtained from calcium salts and sulfuric acid, or to natural gypsum. Thus, Van't Hoff [21] who established the conditions for the changeover of the dihydrate into the semihydrate and the anhydrite, by changing the vapor pressure of the system, came to conclusion that up to 107° there exist all the varieties of calcium sulfate, while from 107 to 170° the semihydrate and anhydrite are the stable forms, at higher temperatures only modifications of the anhydrous form of calcium sulfate can exists. According to Betekhtin[22] and Millon[23] some varieties of the dihydrate may lose half a molecule of water as low as 80-90°, while other forms do not lose the water at this temperature, but lose one and a half molecules of water at 150°. According to the work of Zeidler, which Budnikov quotes [24], both natural as well as synthetic $CaSO_4 . 2H_2O$ on heating in a current of air at 90-96° change into $CaSO_4 \cdot 0.5H_2O$. Chenston and Kundal, according to the same results [24], established that liberation of water from natural gypsum starts at a temperature as low as 40°. According to other results, significant loss of water may occur from the dihydrate even at normal temperatures as long as it is kept in a dry place. The work of Potylitsyn [25] showed that synthetic gypsum dried in a desiccator at 60-65° for several days changed into tne semihydrate.

Budnikov [24] in summarizing the results of various researches, concluded that loss of water from the dihydrate of calcium sulfate startswithin the temperature range 40 to 105° . At 107-128° gypsum loses only part of its water and is converted into the semihydrate. Dehydration starts at 110° in the case of some forms of gypsum, and is complete at 130° . Nevertheless, according to the work of Turuev [26] natural gypsum can change into the semihydrate at 82°; the author points out that under laboratory conditions, spontaneous decomposition of the semihydrate does not occur; the humidity of the air has a decisive effect on the stability of the semihydrate. Conversion of the semihydrate into anhydrite starts at 400°. Within the range 400 to 750° the

TABLE 1

Precipitation of Calcium by Dimethyl Sulfate in the Presence of Dioxane (weighed form $CaSO_4 \cdot 0.5H_2O$)

Calcium taken, mg	Calcium found, mg	Error	
		mg	%
21,00	21,24	+0,24	+1,1
37,05	37,19	+0,19	+0,4
52,50	51.35	−1,15	−2,1
61,75	60,03	−1,72	−2,1
86,45	87,14	+0,69	+0,8
123.50	124,96	+1,46	+1,1

TABLE 2

Precipitation of Calcium by Dimethyl Sulfate in the Presence of Dioxane (weighed form, $CaSO_4$)

Calcium taken, mg	Calcium found, mg	Error	
		mg	%
12,35	12,31	−0,04	−0,30
21,00	20,44	−0,56	−2,50
24,74	24,61	−0,13	−0,50
37,11	37,62	+0,51	+1,00
37,11	36,97	−0,14	−0,37
56,10	55,55	−0,55	−0,90
224,40	221,22	−3,18	−1,40
325,50	320,72	−4,78	−1,40

TABLE 3

Successive Precipitation of Barium and Calcium in Each Other's Presence

Cation det'd	Taken, mg	Found, mg	Error	
			mg	%
Ba^{2+}	13,95	13,81	−0,14	−1,0
Ca^{2+}	123,50	121,14	−2,36	−1,9
Ba^{2+}	32,60	32,48	−0,12	−0,30
Ca^{2+}	217,00	209,88	−7,12	−3,20
Ba^{2+}	40,55	40,90	+0,45	+1,1
Ca^{2+}	54,25	52,96	−1,39	−2,3
Ba^{2+}	48,00	48,34	−0,06	−0,1
Ca^{2+}	325,50	320,72	−4,72	−1,4
Ba^{2+}	40,60	40,43	−0,17	−0,4
Ca^{2+}	324,40	321,22	−3,18	−1,4

water is completely removed and anhydrous calcium sulfate is obtained.

In order to develop a gravimetric method of determining calcium, it is important to know the composition of the precipitated form and of the form in which it is to be weighed, when calcium is precipitated from aqueous solution by dimethyl sulfate in the presence of dioxane. The freshly precipitated form, as studies under the polarizing microscope showed, consists in the main of the semihydrate of calcium sulfate with small inclusions of the dihydrate. When this precipitate is filtered off, washed with alcohol and ether, and dried at 90-100° to constant weight, only the semihydrate is obtained. This was confirmed by repeated observations under the polarizing microscope, and also by the results of x-ray phase structural analysis*.

On drying the calcined precipitate to constant weight at 600-800° anhydrous calcium sulfate was obtained. Studies of this precipitate under the polarizing microscope showed that in the given instance there is formed the β-modification of anhydrous calcium sulfate; this was in complete agreement with the results of Ramsdell and Partridge [27]. This was also confirmed by the method of x-ray phase structural analysis.

Determination of Calcium

a. Weighed form $CaSO_4 \cdot 0.5H_2O$. A neutral or weakly hydrochloric acid solution containing 20-120 mg of calcium is diluted with water to 20-25 ml, 40-50 ml of dioxane is added and the solution heated to 60-70°, and 5 ml of dimethyl sulfate added immediately. (In order to cut down evaporation of the dimethyl sulfate, as indicated already [1], a round-bottom flask containing ice or cold water should be placed over the beaker).

The solution plus the precipitate which has separated out is heated on a water bath or left at 40-50° for 20-25 minutes. The precipitate is filtered through a No. 3 or No. 4 sintered glass crucible, and the filtrate carefully sucked through, the precipitate is washed 2-3 times with dioxane and then with alcohol and ether (it is sufficient to take 10 ml of wash liquor each time), care being taken to ensure as complete removal of filtrate as possible from the precipitate.

After completion of the washing air is drawn through the precipitate for a further 10 minutes. Crucible and precipitate are dried at 90° to constant weight; after cooling in a desiccator, the precipitate is weighed. The calcium is weighed in the form of $CaSO_4 \cdot 0.5H_2O$.

The conversion factor from $CaSO_4 \cdot 0.5H_2O$ to Ca is 0.2755 and to CaO is 0.3857.

Where necessary the dioxane can be recovered. It should be borne in mind that the vapors of dioxane are poisonous, so that experiments with this material should be carried out under a forced draft.

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* The x-ray phase structural analysis of the precipitates prepared was carried out in the x-ray laboratory of the Institute of Chemical Reagents by E. A. Shuga, for which the authors to express their thanks.

Results of the determination of calcium by precipitation of the latter from aqueous dioxane solutions by means of dimethyl sulfate, with subsequent drying of the precipitate at 90° are given in Table 1.

b. Weighed form $CaSO_4$. After precipitating calcium with dimethyl sulfate and holding the precipitate at 40-50° for 20-25 minutes, the precipitate is filtered through a paper filter and washed 2-3 times with dioxane; the precipitate is dried as usual in a porcelain crucible, and then calcined at 600-800°.

From Tables 1 and 2 it is clear that both methods of precipitating calcium with dimethyl sulfate in the presence of dioxane give completely satisfactory results. Saving of time is considerable. It is possible to carry out to to three parallel determinations in one and half hours. The precipitates of calcium sulfate semihydrate and calcium sulfate anhydride obtained are very readily removed from the crucible in the form of compressed sheets, so that preparation of a crucible for further work presents no difficulty.

Determination of Calcium in the Presence of Barium

In the presence of glycerol, precipitation of calcium by dimethyl sulfate from aqueous dioxane solutions is slowed down considerably. This means that it is possible to determine barium and calcium successively as follows.

A neutral solution containing 13-50 mg of barium and 50-300 mg of calcium in the form of chlorides is diluted with water to 70-80 ml, and 5-15 ml of glycerol added, the solution is heated to 60-70° and 5 ml of dimethyl sulfate added dropwise. Heating is continued for another 30 minutes. The precipitated barium sulfate is filtered off through an ashless filter and washed, and is finally calcined at a red heat, or it is filtered through a No. 4 sintered glass crucible and dried at 140°. It is cooled in a desiccator and weighed.

TABLE 4

Determination of Calcium in the Presence of Aluminum and Iron Chlorides, and Hydrochloric Acid (52.50 mg Ca taken).

Foreign salts taken, mg	Ca found, mg	Error	
		mg	%
$FeCl_3$ 180	51,96	—0,54	—1
HCl 2360	51,02	—1,48	—2
$FeCl_3$ 180 $AlCl_3$ 100 HCl 2360	50,64	—1,86	—3

TABLE 5

Composition of the Limestone and Clays

Loss on calcining	SiO_2, %	Fe_2O_3, %	Al_2O_3, %	MgO, %
42,89	1,38	0,68	—	0,30
43,29	1,72	0,21	0,17	1,09
39,41	19,30	4,55	3,10	2,25
—	—	4,57	15,03	4,09

The filtrate and the wash water are evaporated to 20-25 ml, 50 ml of dioxane is added and the solution heated on a water bath to 60-70°. After 15-20 minutes the calcium sulfate is precipitated. The procedure outline above is then followed.

Results for the successive determination of barium and calcium by means of dimethyl sulfate from aqueous glycerol and aqueous dioxane solutions are given in Table 3.

For simplifying and cutting down the time of an analysis, the filtrate can be transferred to a standard flask and precipitation of calcium carried out on an aliquot of this solution.

Determination of Calcium in the Presence of Aluminum, Iron, Ammonium, and Hydrochloric Acid.

As experiment showed, determination of calcium in the presence of large amounts of the chlorides of aluminum, iron, and ammonium is impossible, since the aqueous dioxane solutions separate into layers and the calcium sulfate is not precipitated. When the amount of iron and aluminum chlorides is twice that of the calcium, and the amount of hydrochloric acid is 150 times as much, calcium sulfate is precipitated (a precipitate appears 40-50 minutes after addition of the dimethyl sulfate), but the results obtained are high. Correct results are obtained after reprecipitation. The following procedure is adopted. The calcium sulfate precipitate obtained is filtered through a fine filter paper, and, without washing it, the precipitate is returned to the beaker in which precipitation was first carried out. The precipitate is dissolved in 2 ml of concentrated hydrochloric acid on heating, and the solution filtered; the filter is carefully washed with hot water. The filtrate obtained is diluted to 20-25 ml with water and 50 ml of dioxane added, reprecipitation is then carried out with dimethyl sulfate.

TABLE 6

Determination of Calcium in Limestone and Clay by Means of Dimethyl Sulfate in the Presence of Dioxane

Sample	CaO found by the oxalate method, %	CaO found by the dimethyl sulfate-dioxane method, %	
		Ca weighed in the form $CaSO_4$	Ca weighed in the form $CaSO_4 \cdot 0.5H_2O$
Limestone	52,72	52 20	54,37
•	48,96	47,49	48,63
•	34,91	34,26	32,54
Clay	34,85	31,30	
•	12,56	11,32	

TABLE 7

Precipitation of Strontium with Dimethyl Sulfate in the Presence of Dioxane

Sr taken, mg	Sr found, mg	Error	
		mg	%
19,64	19,46	—0,18	—0,90
29,79	30,19	+0,40	+1 30
39,72	40,11	+0,39	+1,00
49,10	49,50	+0,40	+0,80
79,56	78,28	−0,28	—0,33

Results for the determination of calcium in the presence of aluminum, iron, and hydrochloric acid are given in Table 4.

Determination of Calcium in Limestone and Clay

The method developed for the determination of calcium was applied to samples of limestone and clay readily soluble in hydrochloric acid; the composition of these materials is given in Table 5.

A sample of limestone or clay (about 1 g) is placed in a 100-150 ml breaker and moistened with 5-10 ml of water, the suspension is heated and hydrochloric acid (1: 1) added in small portions until solution is complete. A large excess of hydrochloric acid should be avoided; usually 15-20 ml of acid is sufficient. The solution obtained is diluted to 60-70 ml with water, and is then heated to the boil and filtered through a fine filter paper using paper pulp; the filtrate is collected in a 250-300 ml standard flask. The insoluble residue remaining on the filter is washed 5-6 times hot water + HCl. After cooling, the filtrate is made up to mark with water. 20-25 ml of this solution is then pipetted into a 100-150 ml beaker and heated to 60-70°; 50 ml of dioxane is added followed by 5 ml of dimethyl sulfate. The solution is heated on a water bath for 20-30 minutes. The precipitate which separates out is filtered either through a fine filter paper or through a No. 3-4 sintered glass crucible. In the first instance the precipitate is washed two-three times with dioxane, dried, and then calcined at 600-800°. The form in which the calcium is weighed in this case is $CaSO_4$. In the second instance the precipitate is washed twice with dioxane, and then with alcohol and ether, using 10-12 ml portions; air is then sucked through the precipitate for 10-15 minutes, and the precipitate dried to constant weight at 90°, calcium is weighed in this case as $CaSO_4 \cdot 0.5H_2O$.

Calcium was determined in parallel on the same samples using the classical method [28].

Results for the calcium determinations are given in Table 6.

The method described can be recommended for the rapid analysis of natural samples. The method gives satisfactory results, and is simple and convenient to carry out.

Determination of Strontium. Strontium is usually determined either as the sulfate which is precipitated from a 50% alcoholic medium, or as the oxalate also from alcoholic media. The precipitate obtained is thereupon calcined and either the sulfate or the oxide is obtained. Nevertheless, it is well known [29] that determination of strontium even in the absence of other ions is very complicated and takes a long time.

It was found that dimethyl sulfate in the presence of dioxane, precipitates strontium from aqueous solutions of its salts, in the form of a coarse crystalline precipitate of strontium sulfate.

A neutral solution containing from 20 to 80 mg of strontium in the form of its chloride is diluted with water to 25 ml, 50 ml of dioxane is added and the solution heated to 60-70°; 5 ml of dimethyl sulfate is then added with stirring. After several minutes a crystalline precipitate which readily separates out starts to form. The mixture is heated on a water bath for 15-20 minutes, and, after cooling, the precipitate is filtered through a fine filter; the precipitate on the filter paper is washed 3-4 times with dioxane (10-12 ml each time). The filter paper and precipitate are dried in a crucible and then calcined to constant weight. Strontium is weighed as $SrSO_4$.

SUMMARY

The analytical properties of precipitates can be improved by using the method of "in situ nascendi" reagents. The masking agents present during precipitation, do not merely suppress precipitation of accompanying metals, but also improve the form of the crystals of the salt precipitated. The reason for this is that some of the ions are found in the form of a complex which gradually dissociates.

Methods have been developed for determination of calcium and strontium as their sulfates, the latter being precipitated from aqueous dioxane solutions by means of dimethyl sulfate. Dioxane forms unstable soluble complexes with calcium and strontium chlorides, and depresses the solubility of the sulfates formed. A rapid method is described for determining calcium in the form of calcium sulfate semihydrate or in the form of anhydrous calcium sulfate in the presence of barium, aluminum, iron, and ammonium salts, and also in natural limestone. and clay.

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THE USE OF COMPLEXON III (EDTA) FOR SEPARATING BARIUM, STRONTIUM, AND CALCIUM

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In the work described here, the separation of barium, strontium, and calcium as their sulfates in the presence of EDTA (ethylenediaminetetraacetic acid) was studied, using radioactive indicators. The possibility of such a separation arises on the basis of the following considerations. The stability of the complex compounds of the alkaline-earth metals with ethylenediaminetetraacetic acid differs. According to Schwarzenbach's results [1] the reciprocals of the logarithm of the instability constants of these complexes are 7.76 for Ba, 8.63 for Sr and 10.59 for Ca. The solubility of the sulfates of these metals decreases in the same order. The stability of the complexonates of Ba, Sr, and Ca is so great in an alkaline medium, that not even barium is precipitated as sulfate. On decreasing the pH the stability of the complexonates decreases, and the concentrations of the metal ions in solution increases. It is to be expected that on gradually acidifying a solution containing EDTA and SO_4^{2-} ions, $BaSO_4$ will be first precipitated, since the stability of barium complexonate and the solubility of barium sulfate are less than those for strontium and calcium, and this means that the concentration of ions exceeding the solubility product will be reached sooner. Should precipitation start, then it should proceed quantitatively, since deposition of $BaSO_4$ decreases the concentration of Ba^{2+} in solution, and displaces the equilibrium towards breakdown of the complex. On decreasing the pH further, precipitation of $SrSO_4$ should occur, while calcium which gives a more soluble sulfate and a more stable complex, will remain in solution at this pH.

The results obtained confirmed, in the main, these assumptions.

Experimental Technique. The strontium radioactive indicator used was Sr^{90}, which is in equilibrium with Y^{90}. Since, from a solution containing EDTA, yttrium is not trapped during precipitation of strontium and barium, measurements could be carried out in two ways: 1) by measurements of the activity of the solution on a β-counter on the basis of the increase or breakdown of Y^{90}; 2) measurements of β-activity of Sr^{90} in the precipitates immediately after precipitation, using a torsion counter. We used both these methods.

Ca^{45} was used as the indicator for calcium. The activity of the precipitates was measured by a torsion counter on a type B-2 setup. All the chemical operations were carried out in centrifuge tubes. The total volume amounted to 5-8 ml. Precipitates were separated by centrifugation. The amount of precipitated or coprecipitated element was determined on the basis of activity measurements.

Precipitation of Strontium in the Form of Sulfate. According to Ballczo and Doppler [4] it is impossible to precipitate strontium sulfate quantitatively from solutions containing EDTA; we investigated this point.

Strontium was precipitated at pH about 5 (appearance of the rose color of methyl red), which corresponded to the beginning of this process. To 1 ml of a solution of strontium nitrate containing 10 mg of strontium, was added the radioactive indicator (Sr^{90}), excess of EDTA (2 ml of a 10% solution), a few drops of methyl red, and ammonia until a yellow color was obtained; 2 ml of 10% ammonium sulfate was finally added. The solution was heated on a water bath and carefully acidified with dilute HCl just to the appearance of the rose color of the indicator. The precipitate which separated out was centrifuged and washed twice with 2 ml of wash liquor (100 ml of water, 1 g ammonium sulfate, 1 g of EDTA, and acid to the rose color of methyl red). The activity of the precipitate was measured on a torsion counter. For removing the strontium remaining in solution after the precipitation, 10 mg of strontium in the form of nitrate was added to the solution and then precipitated. The

TABLE 1

Precipitation of Strontium as Sulfate From a Solution Containing EDTA, at pH about 5 (10 mg Sr taken)

Activ. of the precipitates		% Sr in solution	Notes
after 1st ppt.	after 2nd ppt.		
17060	400	2,3	Centrifugated immediately
16600	940	5,4	
17910	364	2,0	
18800	508	2,6	Centrifugated after 2 hours
17520	316	1,8	
18490	340	1,8	
20110	333	1,6	Centrifugated after 24 hours
20970	353	1,7	
22617	367	1,6	

TABLE 2

Separation of Barium and Strontium by Precipitation of $BaSO_4$ from a Solution Containing EDTA, pH about 8.

Taken, mg		Ba : Sr	Activ. of $BaSO_4$		Sr trapped	
Ba	Sr		of the solution	total	in %	in mg
10	10	1:1	205	16330	1,3	0,13*
10	10	1:1	303	19270	1,6	0,16*
10	10	1:1	374	17530	2,2	0,22*
10	10	1:1	38	18210	0,2	0,02
10	10	1:1	72	15730	0,5	0,05
10	10	1:1	40	16980	0,25	0,025
10	1	10:1	42	16820	0,25	0,0025
10	1	10:1	2	16930	0,01	0,0001
10	1	10:1	38	15530	0,25	0,0025
5	50	1:10	0	12850	0	0
5	50	1:10	0	13830	0	0
5	50	1:10	20	15740	0,13	0,065
10	10^{-2}	1:1000	22	15700	0,15	$1{,}5\cdot 10^{-5}$
10	10^{-2}	1:1000	33	16520	0,2	$2\cdot 10^{-5}$
10	10^{-2}	1:1000	0	14210	0	0

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* Without reprecipitation

activity of the second precipitate, expressed as a fraction of the total activity of the first and second precipitates, gives the percentage strontium remaining in solution after the first precipitation. It is clear from Table 1 that even after 2 hours, precipitation occurs to the extent of 97.9% on an average, while on leaving the precipitate overnight precipitation increases to 98.4%. The amount of strontium remaining in solution thereupon is 0.16 mg. Precipitation to this extent can be regarded as fully satisfactory. The incomplete precipitation of strontium sulfate in the work of Ballczo and Doppler [4] can presumably be attributed to the enhanced solubility of $SrSO_4$ in the presence of excess foreign salts added in order to attain the necessary pH [2,3].

Separation of Barium and Strontium.

Ballczo and Doppler [4] showed that separation of barium from strontium is most conveniently carried out by precipitating barium with chromate; we were, however, interested in the sulfate method of separation.

Our first experiments, in agreement with the results of Ballczo and Doppler [1] showed that, when only one precipitation was carried out, an appreciable amount of strontium was trapped by the barium sulfate; in future experiments therefore reprecipitation was carried out.

The work was carried out as follows. To the solution (1-2 ml) containing $BaCl_2$ and Sr nitrate was added the radioactive indicator (Sr^{90}), excess of EDTA, ammonia until its odor was perceptible, and 1-2 ml of 10% ammonium sulfate solution. The solution was heated on a water bath; during this stage, as a result of volatilization of the ammonia, the pH decreased slowly and uniformly. Precipitation of $BaSO_4$ started at a pH of about 8. Further heating on a water bath is perfectly safe, since the drop in pH which thereupon occurs is not sufficient to lead to precipitation of strontium sulfate. This method of lowering the pH is the most convenient technique; on lowering the pH by adding acid, the drop in the pH in individual parts of the solution is too sharp and leads to a partial deposition of strontium sulfate with subsequent trapping with the barium.

After precipitation of the $BaSO_4$ the precipitate was centrifuged and washed twice with 2 ml of wash liquor (100 ml water, 1 g ammonium sulfate, 1 g EDTA, and ammonia to a weak odor). The precipitate was dissolved in an ammoniacal solution of EDTA and the precipitation repeated in the same way. After centrifuging and washing, the precipitate was again dissolved in the ammoniacal solution of complexon, and the solution transferred to a vessel in order to measure its activity. The amount of strontium which was coprecipitated with the barium was determined by comparing the activity of the dissolved barium sulfate and the activity of the solution left after centrifuging. Measurement of the activity of the solutions was carried out on a β-counter on the basis of the increase or breakdown of Y^{90}. The results obtained for various ratios of barium and strontium are given in Table 2. They showed that even after only one precipitation (without reprecipitation) the amount of strontium

TABLE 3

Separation of Strontium and Calcium by Precipitation of Strontium as the Sulfate from a Solution Containing EDTA, pH about 5

Taken, mg		Sr : Ca	Activity		Ca trapped	
Sr	Ca		$SrSO_4$	of the standard	in %	in mg
10	1	10:1	36	7 780	0,5	0,005
10	1	10:1	87	7 780	1,2	0,012
10	1	10:1	40	7 780	0,5	0,005
10	10	1:1	18	7 780	0,25	0,025
10	10	1:1	10	7 780	0.15	0,015
10	10	1:1	20	7 780	0,3	0,03
5	50	1:10	20	7 780	0,3	0,15
5	50	1:10	23	7 780	0,3	0,15
5	50	1:10	28	7 780	0,4	0,2

occluded was only 1.3-1.6% of the amount present (Ba : Sr = 1 : 1); in those cases where reprecipitation was carried out, the amount of strontium trapped did not exceed 0.5% for all the ratios of barium to strontium studied. This means that this method permits the quantitative separation from barium of even micro amounts of strontium. The whole process presents no difficulties and takes 1.5-2 hours.

Separation of Strontium and Calcium. During the separation of the alkaline-earth elements, separation of strontium from calcium causes the greatest difficulties; accordingly, a study of this question is of special interest. The results of the work carried out during the present investigation on the precipitation of strontium sulfate led to the possibility of separating these elements in the form of their sulfates in the presence of EDTA. This possibility was investigated for the following ratios of strontium to calcium: 1 : 1, 1:10, and 10:1. The experimental technique was as follows. To a solution containing strontium nitrate and calcium chloride was added some radioactive indicator (Ca^{45}), excess EDTA, a few drops of methyl red, ammonia to the yellow color of the indicator, and 2 ml of a 10% solution of ammonium sulfate. The strontium sulfate was precipitated by the method described above. The $SrSO_4$ precipitate was centrifuged 2 hours after precipitation. The amount of calcium coprecipitated with the strontium was determined by comparing the activity of the strontium sulfate obtained, and that of a standard which was prepared by mixing exactly the same amounts of radioactive indicator and strontium sulfate as in the test solution. The results obtained (Table 3) show that it is possible to separate strontium and calcium by one precipitation of $SrSO_4$ (without reprecipitation) from a solution containing EDTA. The amount of calcium trapped by the strontium sulfate did not exceed 0.5% of that present for most cases. Only for very low calcium contents did this figure increase to 1.2%; nevertheless, even in this case the error only amounted to 0.01 mg. It should be pointed out that in those cases where the calcium content is considerably greater than that of strontium, even an insignificant amount of calcium present as an impurity can lead to an appreciable error in the determination of strontium. In such cases it is essential to reprecipitate the $SrSO_4$.

SUMMARY

Using the method of radioactive indicators, a study has been made of the possibility of separating barium, strontium, and calcium as their sulfates in the presence of EDTA. In agreement with the results of Ballczo and Doppler [4] it has been established that barium can be quantitatively separated from strontium by precipitating $BaSO_4$ from a solution containing EDTA at a pH of about 8, with a subsequent reprecipitation. The amount of strontium coprecipitated with barium does not exceed 0.5% of that present. Despite what the authors indicated state, it has been established that strontium can be quantitatively precipitated as the sulfate from a solution containing EDTA. A method is suggested for separating strontium and calcium in which strontium sulfate is precipitated from a solution containing EDTA at a pH of about 5. The amount of calcium coprecipitated does not exceed 1.2 % of that present.

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THE APPLICATION OF TRIHYDROXYFLUORONE DERIVATIVES IN PHOTOMETRIC ANALYSIS. DETERMINATION OF SCANDIUM

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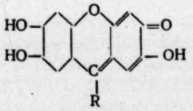
Seeking color reactions for scandium which could be used as the basis of a photometric method of determining this element, we studied some compounds of the orthohydroxyquinone group as potential reagents, individual representatives of this group having already found application in analytical chemistry (chloranilic acid, phenylfluorone, hematein, etc.). In the first instance we tested various derivatives of 2,3,7-trihydroxy-6-fluorone, substituted in the 9-position, whose reactivity towards various metals has been established in the work of Duckert and Gillis et al [1-3], and also in the work carried out in our laboratory [4,5].

Ortho Hydroxyquinones as Reagents for Scandium

Trihydroxyfluorone derivatives  were synthesized from triacetylhydroxyquinone and the respective aldehyde. 0.001 M weakly acid alcoholic solutions were used as reagents; the solutions were prepared by dissolving the requisite amount of compound on moderate heating in 100 ml of 96% ethanol to which 0.5 ml of 6 N HCl has been added. The original scandium solution (1 mg/ml) was prepared by dissolving pure scandium oxide in 1 N sulfuric acid and then diluting with water. This stock solution ,which was 0.01 N with respect to sulfuric acid, was dilute with water to obtain a working solution with the desired scandium content. The reactions were carried out in the presence of a buffer solution within the pH range 1 to 8. The buffer solutions used did not contain any possible precipitants or complexing agents for scandium: chloride, hydrogen phthalate, acetate, glycol, or veronal.

Procedure. To 1 ml of scandium solution was added buffer solution so as to get the requisite pH, the solution was then diluted with water to 4.8 ml and 0.2 ml of reagent solution added. The results obtained are given in Table 1.

Of other compounds containing the orthohydroxyquinone group of atoms, the following compounds were taken: chloranilic acid, hematein, individual representatives of the hydroxy derivatives of the phthaleins, and also compounds of the oxazine group (gallocyanine), and azo derivatives of pyrocatechol which can react in a tautomeric form. The reactions with these compounds were carried out in the same way as with the trihydroxyfluorone derivatives. The results obtained are given in Table 2.

All the reactions described above are not selective for scandium. In a strongly acid medium it is known that trihydroxyfluorone derivatives react with germanium, tin (IV), zirconium, niobium, molybdenum etc.. On lowering the acidity to a pH of 3-7, elements of the third group of the periodic system begin to react: aluminum, gallium, indium, yttrium, and the rare-earths, and also iron (III), thorium, etc.. The selectivity of the other

TABLE 1

Reactions of Scandium with Trihydroxyfluorone Derivatives

Compound number	R	Color of the control solution	Color in the presence of Sc	Optimum pH	Limit of identification, γ
I	Methyl	Yellow	Rose	5,5	1
II	Trichloromethyl	»	»	5; 7,6	0,5
III	Propyl	»	Raspberry	5,6	0,1
IV	Phenyl	»	Rose	7,6	0,2
V	2-Hydroxyphenyl	»	Raspberry	5	0,1
VI	4-Hydroxy-3-methoxyphenyl	»	»	5	0,3
VII	4-Methoxyphenyl	»	Rose	5,6	0,2
VIII	2-Hydroxyl-1-naphthyl	»	»	5	0,3
IX	2-Nitrophenyl	Rose	Raspberry	4	0,3
X	3-Nitrophenyl	Yellow	Rose	7,6	0,3
XI	4-Nitrophenyl	»	»	7.6	0,3
XII	2,4-Dinitrophenyl	Orange	Raspberry	5,6	0,4
XIII	2-Hydroxy-3-nitrophenyl	»	»	5,6	0,2
XIV	4-Hydroxy-3-methoxy-6-nitrophenyl	Yellow	Red	5,6	0,2
XV	4-Dimethylaminophenyl	»	Rose	7,6	1
XVI	2-Methoxy-3,4-methylene-dihydroxy-6-ethyl-β-methylaminophenyl	»	»	5	1
XVII	2,4-Disulfophenyl	»	»	5,6	1

TABLE 2

Reactions of Scandium with Other Ortho Hydroxyquinones

Compound	Color of control solution	Color in the presence of Sc	Optimum pH	Limit of identification γ
Chloranilic acid	Very pale lilac	Lilac	5,6	10
Hematein	Yellow	Rose	5	5
Gallein	»	»	5	1
Cerulein	Dirty violet	Brownish green	5,6	20
Gallocyanine	Blue	Rose	5,6	2
p-Nitrobenzene azopyrocatechol	Yellow	Rose	5,6	1
Stilbazo	Yellow	Rose	5,6	25

orthohydroxyquinones tested is approximately the same. In order to enhance the selectivity of the reaction the technique of masking interfering elements was adopted (aluminum, gallium, indium, iron, yttrium, lanthanum, cerium, zirconium, and thorium). Fluorides, sodium, citrate, oxalate, and pyrophosphate, ascorbic acid, EDTA, diketones and ketoalcohols, sugar, and some other materials, as well as mixtures of these, were tested as masking agents. Only acetylacetone masked all the elements tested, with the exception of iron, when the reagent used was 9-propyltrihydroxyfluorone. 0.1 ml of acetylacetone was sufficient for masking 5 γ of each of the elements listed above, without decreasing the sensitivity of the reaction for scandium.

It is thus clear that all the compounds tested with the orthohydroxyquinone group react with scandium. They do not give fluorescent reactions with scandium. The most sensitive reagents are 2, 3, 7-trihydroxy-6-fluorone derivatives; of these the most sensitive reagent for scandium, with respect to sensitivity and specificity (in the presence of acetylacetone), is 9-propyl-2,3,7-trihydroxy-6-fluorone (henceforth called propylfluorone). A comparison of the absorption curves of solutions of the compounds studied and of their complexes with scandium showed that propylfluorone is the most suitable for the spectrophotometric determination of scandium, since the superposition of the absorption curves of the reagent itself and of the complex with scandium least when this reagent is used. Another reagent which is equal in sensitivity to propylfluorone is o-hydroxyphenyltrihydroxyfluorone; nevertheless this compound is not so selective as propylfluorone, and does not permit masking of interfering elements without simultaneous masking of scandium. We chose propylfluorone for the quantitative determination of scandium.

Effect of pH. Propylfluorone in weakly acid or neutral media (pH 3-7) forms a red compound with scandium ions, this compound being precipitated when the scandium content is high.

Solutions of this compound are stabilized by gelatin. Weakly acid, dilute solutions, of propylfluorone have a yellow color with a yellowish-green fluorescence. In Fig. 1 is shown effect of pH changes on color development The solutions were 4×10^{-5} M with respect to propylfluorone and 12×10^{-5} M with respect to scandium. In order to stabilize the solutions, 0.5 ml of a 1% gelatin solution was added for a total volume of 25 ml; this was done in all subsequent experiments. The optical density was measured in a Pulfrich photometer using a 10 mm cell, water was the reference solution, and measurements were carried out at 530 mμ 30 minutes after preparing the solutions. As the curve shows, the maximum color develops at pH 5.6. At pH greater than 6 the optical density of solutions of the reagent increases sharply.

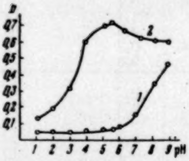


Fig. 1. Relation between color intensity and pH.: 1) reagent; 2) scandium complex.

Absorption curves of solutions of the reagent and of the complex, measured on a SF-4 spectrophotometer are shown in Fig. 2. The solutions were 2×10^{-5}M with respect to propylfluorone, and, in the case of the complex, 6×10^{-5}M with respect to scandium. Optical density measurements were carried out in a 5 mm cell against water, and were made 10 minutes after preparing the solutions. Maximum light absorption by reagent solution is observed at 480 mμ, while maximum light absorption by the complex is observed at 510 mμ. For this work it is convenient to use a light filter with maximum transmission at 530 mμ where the absorption of the complex is still high enough, while the reagent only absorbs to a small extent.

Composition of the Complex. In order to establish the molar ratio of propylfluorone to scandium in the complex, the Ostromyslensky-Job method, and the method of molar ratios [6, 7] were used.

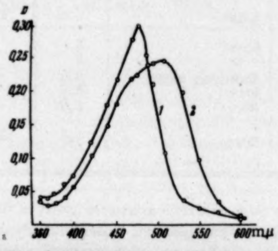


Fig. 2. Absorption curves: 1) reagent 2) scandium complex.

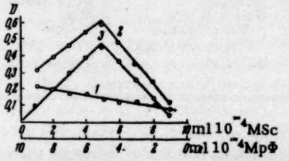
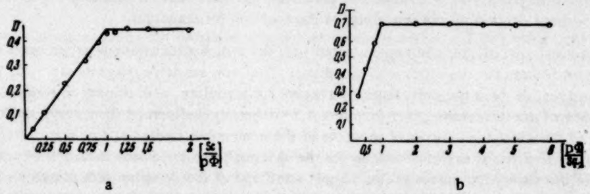


Fig. 3. Method of continuous changes: 1) reagent; 2) experimental results; 3) corrected results.



a

b

Fig. 4. Method of molar ratios: a) propylfluorone concentration constant; b) scandium concentration constant.

For the continuous-change method, the solutions used ranged from 0.4×10^{-5} to 3.6×10^{-5}M with respect to scandium, and from 3.6×10^{-5} to 0.4×10^{-5}M with respect to propylfluorone. Optical density measurements were carried out in a 10 mm cell against water, measurements were made at 530 mμ 2 hours after preparing the solutions. Measurements after 3, 4, and 5 hours have the same values for the optical density. Results of these measurements are given in Fig. 3.

Experiments were carried out by two variants for the molar ratio method: a) the propylfluorone concentration was kept constant at 2×10^{-5}M while the scandium concentration was varied from 0.1×10^{-5} to 4×10^{-5}M; b) the propylfluorone concentration was changed while the scandium concentration was kept constant. A correction was applied for the light absorbed by excess propylfluorone, the correction being determined by measuring the optical density of the corresponding solutions in the absence of scandium. The results obtained are given in Fig. 4a and 4b.

As is clear from Fig. 3, 4a, and 4b, the experimental results for both the optical methods indicate that only one complex is formed under the conditions used, and that this complex has a molar ratio of scandium to reagent of 1:1.

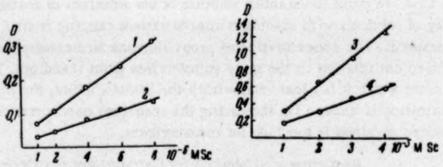


Fig. 5. Relation between optical density and scandium concentration. 1) 20 mm cell; 2) and 3) 10 mm cell; 4) 5 mm cell.

TABLE 3

Determination of the Equilibrium Constant (t°=20°; 1= 10 mm; standing time 2 hours).

Expt. No.	$C_{Sc} \times 10^5$	$C_{Sc} = C_{H\Phi}$		$C_{Sc} < C_{H\Phi}$		K'
		$C_{H\Phi} \times 10^5$	E	$C_{H\Phi} \times 10^5$	E_{max}	
1	1	1	0,31	6	0,34	$1,10 \cdot 10^7$
2	2	2	0,60	6	0,63	$1,90 \cdot 10^7$
3	3	3	0,88	6	0,92	$1,26 \cdot 10^7$
					Mean	$1,42 \cdot 10^7$

On the basis of the results obtained, and also on the assumption that the reactive group of atoms in propylfluorone is the orthohydroxyquinone group, the structure of the scandium complex can be regarded as similar to the structure of the phenolfluorone complex of antimony [4].

Equilibrium Constant. For calculating the apparent equilibrium constant of the reaction $ScO^+ + H\Phi \rightleftharpoons ScO$ + H^+ the same method was adopted as that used for calculating the equilibrium constant of the reaction for the formation of antimony phenylfluoronate [4]. Calculations were made on the basis of the formula $K' = x/(c-x)^2$ if we let $x = Ec/E_{max}$ where x is the equilibrium concentration of the complex in solution, c is the total concentration of scandium in solution, E is the optical density for a stoichiometric ratio of scandium to propylfluorone and E_{max}, is the optical density when excess propylfluorone is present. Results of these experiments are given in Table 3.

The equilibrium constant was also calculated by the Schaeppi-Treadwell method [8] from the results obtained during a study of the composition of the complex by the continuous change method (Fig. 3). At the point corresponding to the ratio Sc:H Φ = 1:1, the optical density was 0.44. The intersection point for the composition curves corresponded to an optical density of 0.46. The equilibrium constant of the reaction calculated from these results is 2.05×10^7.

The high value of the equilibrium constant indicates that the propylfluorone complex of scandium is highly stable. This constant can be used for calculating the requisite excess of reagent for the photometric determination of scandium; calculations show that in order to complex 99% of scandium as the colored complex it is sufficient to use a twofold excess of the reagent this was confirmed experimentally.

The molar extinction coefficient was determined for a wavelength of 530 mμ. Experiments were carried out for different scandium concentrations ($1-3 \times 10^{-5}$M) and a constant propylfluorone concentration (6×10^{-5}M), so that the ratio of their concentrations varied from 1:2 to 1:6. The mean value of the molar extinction coefficient was found to be 32,000.

When excess propylfluorone is used, and the pH is 5.6, the color reaches a maximum in as little as 5 minutes and does not change in the course of several hours.

Conformation to Beer's Law. In order to establish whether or not solutions of scandium propylfluoronate follow Beer's Law, the optical density of solutions with scandium concentrations ranging from $1 \times 10^{-8} - 8 \times 10^{-6}$M and $1 \times 10^{-5} - 4 \times 10^{-5}$M was measured. The concentration of propylfluorone was correspondingly 2×10^{-5} and 8×10^{-4}. Measurements were carried out relative to the same solution free from scandium. The results obtained are given in Figs. 5a and 5b, from which it is clear that, within the limits studied, the relation between color intensity and scandium concentration is linear. On increasing the scandium concentration above 5×10^{-5}M, the optical density of the solutions obtained is too high for measurement.

TABLE 4

Determination of Scandium in the Presence of Other Elements (3γ of Sc taken, 0.1 ml of acetylacetone added)

5γ of each metal added	Sc found, in γ
Al	3,1
Y	3,0
La	3,0
Ce	2,9
Th	3,0

Recommended Method for Carrying out the Determination. Into a 26 ml standard flask is introduced 1-10 ml of a weakly acid (not more than 0.005 N acid) test solution, so that after dilution to the mark, the scandium concentration lies within the limits 1×10^{-6}M (0.045γ Sc/ml) to 8×10^{-6}M (0.38γ Sc/ml). 0.5 ml of a 1 gelatin solution and 5 ml of a 0.003% solution of propylfluorone is added. The contents of the flask are then mixed and made up to the mark with an acetate buffer whose pH is 5.6, the solution is mixed again and then left for 10 minutes. The optical density is measured at 530 mμ relative to a control solution, in a 20 mm cell.

For determining the scandium concentration within the limits 0.4γ/ml to 2γ/ml, 2 ml of a 0.03% solution of propylfluorone is taken, and the optical density measured in a 5 or 10 mm cell. The order in which the solutions are added is the same.

Color intensity can also be measured visually by the method of standard series, or by using a colorimeter with a light filter e. g. the KOL-1M colorimeter

The 0.003% solution of propylfluorone should be prepared from the 0.03% solution by dilution with ethanol.

Table 4 contains results obtained during the determination of scandium in the presence of some interfering elements. The experiments were carried out as described above, but 0.1 ml of acetylacetone was added to the solutions.

SUMMARY

Compounds containing the orthohydroxyquinone group give color reactions with scandium. 2, 3, 7-Trihydroxy-6-fluorone derivatives are the most sensitive reagents. 9-Propyltridhydroxyfluorone permits detection of scandium at a dilution of $1:5 \times 10^7$, and is suitable for the photometric determination of 0.04γ/ml of scandium. Solutions of the scandium complex conform to Beer's law.

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AN INDIRECT PHOTOMETRIC DETERMINATION OF CYANIDE BY MEANS OF DIVALENT MERCURY AND DYPHENYLCARBAZONE

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We have developed a method for the direct photometric determinations of cynanide which is based on the color reaction of divalent mercury ions with diphenylcarbazone. The hydrogen cyanide liberated is absorbed by a solution of mercuric chloride. Only that part of the divalent mercury which has not reacted with cyanide reacts with diphenylcarbazone. The method is similar to one developed earlier with p-dimethylaminobenzylidenethiocyanate [1,2]. Divalent mercury ions, under the appropriate conditions, react with diphenylcarbazone to form a colloidal solution with a violet color. Diphenylcarbazide gives exactly the same color, since it is readily oxidized to diphenylcarbazone by atmospheric oxygen [3-6]. During a study of the reaction of both these reagents with divalent mercury, Alekseev [7] concluded that diphenylcarbazone is the most suitable reagent for the photometric determination of divalent mercury, since it can be obtained in a purer form, while the color developed is more stable. The reaction between divalent mercury and diphenylcarbazone is more sensitive than and is not so dependent on the experimental conditions, as the reaction of mercury with p-dimethylaminobenzylidenethiocyanate. In this respect therefore the new method is better than the one suggested previously.

Apparatus and Reagents. 1. Universal Coleman Spectrophotometer, Model 14, cell 14-307.

2. Conway Diffusion Apparatus (Microchemical Specialties) 172-A. Packing grease: vaseline + paraffin (1:2), m.p. 40°.

3. Approximately 0.1 M potassium cyanide. The molarity of the solution was determined by the usual method [8]. A solution with the requisite concentration was prepared prior to use by dilution.

4. A saturated aqueous solution of tartaric acid.

5. Buffer solution (pH 4.00). 800 ml of 0.2 M acetic acid was mixed with 200 ml of 0.2 M sodium acetate.

6. 1% alcoholic solution of diphenylcarbazone. The solution was filtered after standing overnight.

7. Mercuric chloride solutions. An aliquot of salt sufficient to give a solution with a concentration of 500γ of Hg^{2+}/ml was dissolved in the appropriate volume of buffer solution. By diluting this solution with buffer solutions, solutions with the following concentrations were prepared: 0.50; 1.00; 1.50; 2.00; 2.50, and 3.00γ Hg^{2+}/ml.

Reaction Conditions. Alekseev [1] carried out the color reaction at pH 7. We chose a pH of 4 (buffer solution) since at this pH absorption of the reaction products is a maximum. Absorption decreases with time, but measurements carried out after 5 minutes gave good reproducibility. The optical density was measured at 550 mμ; at this wavelength interference from excess reagent is a minimum (Fig. 1).

In order to establish the necessary amount of reagent, 10 ml of buffer solution containing from 0.5 to 3.0 γ Hg^{2+}/ml was taken, and 0.1 and 0.2 ml of diphenylcarbazone solution added. Higher values were obtained for the optical density on using 0.2 ml of reagent (Fig. 2). Beer's law held up to concentrations of 3.0 γ Hg^{2+}/ml. Addition of a large volume of reagent led to coagulation. Temperature variations within the limits of 15-25° had no effect on the optical density.

Experimental Procedure. By means of a pipet, 5 ml of a buffer solution containing 3.00 γ Hg^{2+}/ ml was introduced into the inner cell of the Conway diffusion apparatus, while 5 ml of a solution containing from 0.30 to 3.5 γ of CN^- was introduced into the outer cell. The apparatus was then sealed. 1 ml of the saturated tartaric acid solution was then taken up in a pipet, and the lid of the apparatus shifted horizontally so that an opening was formed over the outer cell sufficient to introduce the tip of the pipet; the tartaric acid solution was then rapidly introduced into the cell. The lid was then replaced and the solutions transferred into the outer cell by gently rocking the apparatus. It was then allowed to stand long enough for absorption to take place (4 hours at a room temperature of 20°). The lid was then removed. 0.1 ml of diphenylcarbazone solution was pipetted into the inner cell and the solution mixed with a glass rod. The solution was then transferred by means of a pipet into the spectrophotometer cell and the light absorption measured at 550 mμ 5 minutes after the color had developed. The blank solution used was a buffer solution to which reagent had been added.

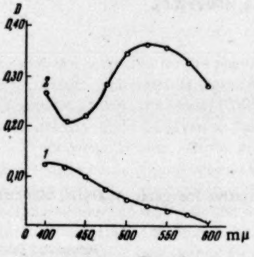

Fig. 1

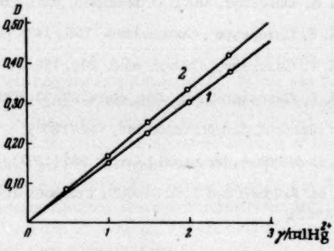

Fig. 2

Fig. 1. Absorption curves: 1) buffer solution not containing divalent mercury but containing 0.2 ml of reagent per 10 ml of solution; 2) buffer solution containing 2γ Hg^{2+}/ml and 0.2 ml of reagent per 10 ml solution.

Fig. 2. Absorption curves illustrating the effect of excess reagent: 1) on addition of 0.1 ml of reagent; 2) on addition of 0.2 ml of reagent.

A standard curve was prepared in the same way using solutions of potassium cyanide containing from 0.3 to 3.5 γ CN^-. This curve was a straight line. The standard curve can be constructed directly as well (without the microdiffusion stage).

Determination of Cyanide

CN^- taken, γ / 5 ml	CN^- found, γ/ 5 ml
0,30	0,300; 0,308; 0,292; 0,300; 0,300
0,50	0,508; 0,500; 0,492; 0,500; 0,492;
1,00	1,008; 1,000; 1,012; 1,002; 0,998
2,00	2,000; 2,008; 2,000; 1,992; 2,000
3,00	3,008; 3,000; 3,000; 2,992; 3,008
3,50	3,516; 3,500; 3,492; 3,484; 3,508

The table contains results obtained during the determination of various amounts of cyanide. Interference from sulfide ions can be eliminated by precipitation with cadmium nitrate [2].

SUMMARY

An absorptiometric method for the indirect determination of cyanide based on the color reaction of mercuric ions with diphenylcarbazone has been developed. Hydrogen cyanide is liberated by microdiffusion and is absorbed by a mercuric chloride solution. Orly excess mercuric ions which have not been complexed by the cyanide is able to react with the diphenylcarbazone.

The method permits determination of 0.30-3.50 γ CN^-/ 5 ml. Separation of the cyanide by microdiffusion facilitates control of the acidity of the medium prior to carrying out the color reaction, and so eliminates the effect of foreign salts and prevents interference from halide and thiocyanate ions. Interference from sulfide ions can be prevented by precipitation with cadmium nitrate.

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PHOTOMETRIC DETERMINATION OF MICROAMOUNTS OF THORIUM

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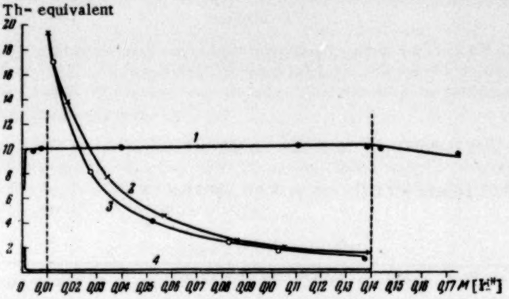
Among the reagents suggested for the photometric determination of micro amounts of thorium, the one which has found the widest application is thoron which was suggested by Kuznetsov [1, 2] and was first used for this purpose by Thomason, Perry, and Byerly [3]. During the analysis of samples containing microgram amounts of thorium, serious attention must be given to the concentration of the thorium and to its separation from elements which interfere with its determination. Of the methods used for concentrating micro amounts of thorium the most widely used ones are those based on coprecipitation of thorium with the hydroxides of iron [4-7] and aluminum [8-10]. An interesting method of concentrating thorium from natural water has been suggested by Taylor and Dillon [11], who coprecipitated thorium with calcium oxalate from 1.5 liters of water acidified with HCl. However, they did not study the completeness of coprecipitation of thorium with the precipitate of CaC_2O_4, so that to talk about the practical suitability of this method for concentrations purposes is out of the question. For removing thorium from elements which are precipitated at the same time as it on $Fe(OH)_3$, and which interfere with its photometric determination, several chromatographic [12-13], and extraction [7, 14-18] methods have been suggested. Of the methods based on coprecipitation of thorium with carriers, the most well known are the fluoride [7, 19-20] and oxalate methods [6, 19, 21]. Cerium or lanthanum are used as carriers. But, since these elements interfere with the photometric determination of thorium, them in some cases it is more expedient to precipitate thorium on calcium oxalate. Unfortunately, there is very little data available on this problem [9,11].

A number of papers have been devoted to the determination of thorium in several natural and synthetic samples, in monazite [15, 22], zircon, cassiterite, and other minerals [16], and in magnesium alloys [23]. In the work described in these papers all the operations of separating thorium from interfering elements were carried out with macro amounts of thorium (1-5 mg), and only in the last stage of the photometric determination was an aliquot part containing 20-100 γ Th taken.

In the work of Goldberg and Piccioto [7] and that of Tilton, Aldrich, and Inghram [6], the yield of thorium was controlled by means of the indicator UX_1. In these cases thorium was precipitated on LaF_3 or $La_2(C_2O_4)_3$, and then separated from the carrier by means of extraction.

In a paper by Taylor and Dillon [11] devoted to the development of a method for the determination of thorium in water thorium was precipitated with calcium oxalate directly from the total volume of test water. The precipitate of oxalates was calcined, dissolved in hydrochloric acid, and then the thorium determined photometrically. The amount of thorium in samples has been determined by the so called spike method. This method is fairly accurate as long as the requisite conditions are followed, but it increases the difficulty of determination. Furthermore, it is only applicable in those cases where the percentage precipitation of thorium on calcium oxalate in two samples is exactly the same (independently of the absolute extent of the percentage coprecipitation). However, completeness of coprecipitation was not established, and the possibility is not excluded that it is variable. Most methods have been developed for the determination of 20-100 γ of thorium; accordingly, such methods cannot be used for determining smaller amounts of thorium (of the order of 1-10 γ) without preliminary experimental checking.

In this connection we have developed a method for determining γ amounts of thorium which takes into account the possible presence of the alkali and alkaline-earth metals, U, Fe, and the rare-earths.



Relation between the extent of the absorption of solutions containing Th, Ce, La, and thoron, and the acidity of the hydrochloric acid solution 1) 10 γ Th; 2) 2 000 γ Ce; 3) 2 000 γ La; 4) thoron solution (about 0.003 %).

The reagents used (chemically pure grade), as a rule, were not given a supplementary purification, since their thorium content was below the limit at which it could be detected photometrically. The solutions were prepared from ordinary distilled water, and, after preparation, were acidified to a pH of about 1.

Thorium was determined on the basis of calibration curves. The optical density of the solutions was measured on a FÉK-M photocolorimeter (green-light filter). In order to increase the reliability and accuracy, measurements were made in one cell, i. e., the total absorption of the solution and cell was determined with respect to air. During measurements of the optical density by this method it is easy to achieve good reproducibility for the scale deflections (the error amounts to 0.001-0.002 on the optical density scale), we were unable to obtain such reproducibility when using three cells (the error in the readings amounted to 0.01).

An increase of 1 γ in the amount of thorium in solution gave an increase of 0.010 in the optical density (E) under the conditions used for carrying out the photometric reactions.

The requisite amount of thoron, in the form of a solution, was introduced into a specially prepared, accurately graduated measuring cylinder, the solution containing thorium was then added and the volume made up to 15 ml by adding acid of the requisite concentration. After mixing, the solution was transferred to the cell and its optical density measured several times (it was shown in separate experiments that equilibrium is reached in solution during the time the solution is being prepared).

Conditions for Carrying out the Colorimetric Reaction.

Optimum Thoron Concentration. According to published results, the optimum concentration of thoron in the solution being measured photometrically is 0.01% for a wide range of thorium concentrations. According to our experiments, for work under the conditions we adopted, this concentration should be lowered to 0.002-0.003% for the determination of 1-20γ of thorium. At a concentration of 0.004% of thoron an appreciable deviation from Beer's law occurs. For all our determinations the thoron concentration was 0.003% (more accurately 0.0029%).

The Effect of Acidity on the Absorption of the Complexes of Thoron with Thorium, Cerium, and Lanthanum.

There is a large divergence of opinion in the published literature on the optimum pH to be used. Accordingly, we studied the relation between the light absorption of solutions of the complex and the hydrochloric acid concentration. The results obtained for a complex containing 10 γ of Th, and also the values for the absorption of solutions (in units of the equivalent of thorium) containing 2000 γ Ce and 2000 γ La, and of solutions containing

TABLE 1

Effect of Calcium on the Absorption of Solutions Containing Various Amounts of Thorium

Taken		Found	Taken		Found
Ca, mg	Th, γ	Th, γ	Ca, mg	Th, γ	Th, γ
5	0	0	25	0	0,2
	10,0	10,0		5,0	5 3
	20,0	20,0		20,0	20,0
10	0	0	50	0	0,7
	1,0	1,0		2,0	2,5
	10,0	10,1		10,0	9,9
	20,0	20,1	100	0	1,3
				10,0	9,0

only thoron, as a function of the acidity is shown in the diagram. It is clear from these results that the light absorption of solutions containing only thorium remains constant on changing the pH from 2.3 to 0.85. Outside this pH range there is considerable weakening of the color. Since interference from the rare-earths, and possibly from other ions, increases with increasing pH, the acidity of the solution should be as high as possible. In our work the acidity of the solutions being measured photometrically varied from 0.11 to 0.14 N (pH 0.96-0.85).

Effect of Calcium Ions on Thorium Determination.

In order to establish the possibility of determining thorium in the presence of calcium, the effect of various amounts of calcium on the absorption of solutions containing thorium (Table 1) was studied.

From these results it is possible to draw the conclusion, which is important from a practical viewpoint, that small amounts of calcium (5-10 mg) do not cause any distortion of the results during determination of 0-20γ and more of thorium.

Coprecipitation of Thorium with Ferric Hydroxide.

Coprecipitation of thorium with Fe (OH)$_3$ was adopted for separating it from Na, K, Ca, Ba, and other metals, and for simultaneously concentrating it. Experiments carried out to establish the completeness of precipitation of thorium showed that 10^{-6} - 1000 γ of thorium can be quantitatively coprecipitated with Fe(OH)$_3$. The yield, which was determined by means of the indicators UX$_1$ and RdTh, varied around 100 %, only rarely dropping down to 95 %.

Preparation of a Solution of UX$_1$ Indicator.

In order to prepare a solution of the indicator almost free from U, Fe, and other metals we adopted the following method for separating UX$_1$ from $UO_2(NO_3)_2$. A concentrated solution of $UO_2(NO_3)_2$ which was 1N with respect to HNO_3 and was saturated with NH_4NO_3 was shaken 6-7 times with ether. The aqueous layer was transferred to a porcelain beaker and the solution evaporated to dryness, the residue was then slightly calcined to remove ammonium salts. The calcined residue was dissolved in concentrated HNO_3 and the solution transferred to a 50 ml beaker in which it was evaporated to dryness on a water bath. The residue was dissolved on boiling in 10 ml of water and 10 ml of a 10% solution of $H_2C_2O_4$, to this solution 10 mg of Ca^{2+} was added. When no precipitate separated out another 5 mg of Ca^{2+} was added. After 6-12 hours the precipitate was filtered off (centrifuged) and washed several times with a 1% solution of oxalic acid, it was finally washed once with water and calcined for 60 minutes at 600°. The calcium oxide obtained was dissolved in a few ml of 3.6% (1: 10) HCl, and the solution filtered through a Schott No. 4 filter and diluted to about 100 ml with 0.1 N HCl. The yield of UX$_1$ obtained as a result of the operations described above varied within the limits of 60-90%. The indicator solution prepared from the UX$_1$ purified in this way was almost free from carrier and contained traces of uranium which does not interfere with the photometric determination of thorium. 1-2 ml of this solution with an activity of 1500-2000 impulses / minute was taken for each analysis.

TABLE 2

The Relation between Completeness of Coprecipitation of Thorium with Calcium Oxalate and Various Precipitation Conditions

Taken			Acid concentration	Ca introduced	Ppt. contact time	UX_1 found in the filtrate, (%)
Th, γ	Ca, mg	other elements				
20	1,25	—	0	Before addition of $H_2C_2O_4$	12 Hours	5,8
10	5	—	0	» » »	12 »	1,6
10	5	—	0	Into the hot oxalic acid solution	12 »	0,5
10	5	—	0,15 *N* HCl	Before addition of $H_2C_2O_4$	12 »	3,7
10	5	—	0,15 » »	Into the hot oxalic acid solution	12 »	0,5
20	10	—	0,15 » »	Before addition of $H_2C_2O_4$	15 Days	16,4
20	10	—	0,15 » »	Into the hot oxalic acid solution	15 »	10,1
20	10	Fe 10mg	1,5 *N* CH_3COOH	Ditto	12 Hours	0,2
10	10	U 780 γ	0	» »	12 »	0,6
2	10	Fe 10mg U 2100 γ	Ce 50 γ	» »	12 »	1,1

Separation of Thorium from Iron and Uranium by Precipitation on Calcium Oxalate.

For removing thorium from U, Fe, and other metals which form soluble compounds with the oxalate ion, we developed a method for coprecipitating thorium with calcium oxalate from small volumes of weakly acid solutions. The procedure adopted was as follows. To the solution containing Th, U, Fe, etc. was added a known amount of indicator, and the solution evaporated to dryness in a 25-50 ml beaker on a water bath, (in the general scheme of analysis this solution is obtained on dissolving the $Fe(OH)_3$ in 3.6% hydrochloric acid), the residue was dissolved in a small amount of dilute hydrochloric acid and a few ml of water and 10% $H_2C_2O_4$ solution added, 5-10 mg of Ca^{2+} was finally added to the hot solution. After several hours the precipitate of calcium oxalate was removed from the solution by centrifuging, calcined at a definite temperature, and dissolved in a known amount of HCl; this solution was filtered through a Schott No. 4 filter and was used for the photometric determination, after which the yield of UX_1 was established.

Study of the Completeness of Coprecipitation of Thorium with Calcium Oxalate under Various Conditions.

The experiments carried out to establish the extent of the coprecipitation of thorium with calcium oxalate were carried out in the same way as that described for the general scheme of analysis; completeness of coprecipitation of thorium was determined by measuring the amount of UX_1 remaining in solution after filtering and washing the oxalate precipitate.

Preliminary experiments showed that the extent to which thorium is coprecipitated with calcium oxalate is independent (within the limits studied) of the volume of solution from which precipitation is carried out, and of the amount of $H_2C_2O_4$. In these experiments the volume was varied from 6 to 20 ml, while the relative amount of $H_2C_2O_4$ was varied from 20 to 60% (ml of 10% solution). Accordingly, in our subsequent experiments we chose the most convenient volume from a practical viewpoint, namely 9-11 ml, the oxalic acid content if which corresponded to 4 ml of a 10% solution of $H_2C_2O_4$.

It was established that it is quite satisfactory to wash the precipitate twice with a dilute solution of oxalic acid (25 g/liter), and once with water, 5 ml portions being used each time. Washing was carried out with cold solutions.

The relation between the completeness of precipitation of thorium on calcium oxalate was studied as a function of: the acidity of the solution, the amounts of calcium and thorium, the order of mixing the solutions of calcium chloride and oxalic acid, the presence of Fe, U and Ce in solution, and the time elapsed from the moment of precipitation to the removal of the precipitate from solution. The most characteristic results of these experiments are given in Table 2.

From the adduced results it is clear that completeness of coprecipitation with CaC_2O_4 is almost independent of the amount of Th and Ca in solution, apart from the smallest amount of calcium taken (1.25 mg) when the loss of thorium amounts to 6%. It is obvious that 10 mg of carrier is completely sufficient for almost complete quantitative separation of 1-20 γ of Th from solution.

Changes in the acidity of the solution from 0 to 0.15 N with respect to HCl also have no effect on completeness of precipitation of thorium. But, since at an acidity of 0.15 N, calcium oxalate is precipitated with great difficulty, we chose an acidity of about 0.04 N with respect to HCl.

In certain cases coprecipitation of thorium with CaC_2O_4 from concentrated acetic acid solution may be interest.

The presence of the foreign ions studied in solution has little effect on the completeness of coprecipitation of thorium. Completeness of coprecipitation of thorium depends to a somewhat greater extent on the order of mixing of solutions of $CaCl_2$ and $H_2C_2O_4$, and the time for which the precipitate is allowed to stand in contact with the solution; this can be explained by the absorption mechanism of the coprecipitation of thorium with CaC_2O_4. On adding the carrier to hot oxalic solutions, the CaC_2O_4 precipitate formed traps thorium better than during precipitation from calcium-containing solutions to which oxalic acid is added. Obviously, in the first instance finer crystals with a larger surface are formed which strongly absorb thorium. On standing, the crystals of calcium oxalate get larger, their surface decreases, and completeness of coprecipitation of thorium with them decreases.

In practice the precipitate of calcium oxalate settles out completely in a few hours, and in our method is separated from solution by centrifuging 6-12 hours after precipitation.

Conditions for Treating the Precipitate of Calcium Oxalate

In order to remove the calcium oxalate precipitates from solution we adopted centrifuging instead of filtration which is more practical and convenient, since we did not wish to introduce any additional contamination into the solution. We found that filter paper ash sometimes led to considerably turbidity of the solution, and that certain ashless filter papers (particularly blue band) contain an appreciable amount of iron.

Centrifuging was carried out at 2000 revolutions/minute in 15 ml quartz tubes. 0.5-1 ml of alcohol was poured onto the aqueous layer before centrifuging otherwise a film of the precipitate remained on the water surface. After centrifuging and washing, the precipitate of CaC_2O_4 was calcined at 600-650° for 60 minutes. It was found that precipitates calcined at a lower temperature gave turbid solutions when the residue was dissolved. Precipitates calcined at a higher temperature were more difficult to dissolve in hydrochloric acid, leading therefore to an increase in thorium loss. The CaO residues obtained were dissolved in 1 ml of 3.6% HCl on boiling (the residue dissolved without heating after 1-2 hours). The solutions obtained in this way always contained some mechanical impurities (dust falling in at various stages; particles formed during calcination of the oxalate; SiO_2 which often gets into these solutions during the analysis of mineral samples) so that these solution had to be filtered through No. 4 small-size Schott filters. Not more than 5% of thorium was lost on the filter during this stage, and the solutions obtained were, as a rule, completely clear. The filtrate was collected in a small beaker, and the filter washed 2-3 times with 0.1 N HCl, the washings being collected in the same beaker until the total volume was 10-12 ml. The solution was then transferred to a measuring cylinder, the thoron solution was added and the solution measured photometrically. After the absorption had been measured the solution was transferred to a 40 ml cell and its β-activity measured on an AS-2 counter.

Analysis of Synthetic Samples. In order to check the method developed, a large number of synthetic samples containing various amounts of thorium and various interfering elements were analyzed. Results of these experiments are given in Table 3.

It is clear from these results that in some cases the results are somewhat high, obviously because of the thorium content of the indicator solution. The extent of this increase, which was carefully determined after preparing each new indicator solution, was taken into account during calculation of the results for the analysis of Th-containing materials.

The mean absolute error during determination of thorium in synthetic and other samples varied around 0.3 γ Th. The maximum absolute error was taken to be 0.5 γ.

TABLE 3

Determination of Thorium in Synthetic Samples

Taken		Yield of UX_1	Th found	Error	Taken		Yield of UX_1	Th found	Error
Th, γ	other elements, mg	%	γ		Th, γ	other elements mg	%	γ	
0	—	—	0,1	+0,1	10	—	99	9,5	—0,5
0	Fe^{3+} 10	—	0,2	+0,2	25	—	94	24,8	—0,2
0	Fe^{3+} 10; 2	—	0,3	+0,3	10	U 17	96	10,3	+0,3
0	—	96	0,2	+0,2	10	Fe^{3+} 10	95	9,5	—0,5
2	—	92	1,9	—0,1	5	Fe^{3+} 10; U 2	95	4,8	—0,2
5	—	96	5,2	+0,2	15	Fe^{3+} 10; U 2	96	15,2	+0,2

Note. 10 mg of Ca was used for coprecipitating the Th.

TABLE 4

Determination of Thorium in the Presence of Cerium

Taken		Q_1	Q_2*	$H*_1$	H_2*	Th found, γ	Error, γ
Th, γ	Ce, γ						
10	2000	11,0	14,0	0,140	0,023	10,5	+0,5
10	2000	11,2	15,0	0,143	0,027	10,5	+0,5
10	6000	10,2	15,4	0,159	0,027	10,1	+0,1
10	6000	9,5	15,2	0,159	0,025	9,5	—0,5

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* H_1 and H_2 are the initial and final acidities of the solution being measured photometrically; Q_1 and Q_2 are the amounts of thorium corresponding to the optical density of the solution found at the initial and final acidity.

During accurate and careful work, the observed deviations of the results obtained from the true values rarely exceeded the value of the maximum absolute error. This accuracy is quite permissible for the determination of 2-10 γ and more of thorium. During the determination of smaller amounts of thorium it is necessary to take special precautions in order to decrease the value of this error.

Determination of Thorium in the Presence of the Rare-Earths.

When the method described is used for the separation of thorium from certain interfering elements, the rare-earths are precipitated together with thorium on the calcium oxalate, and, since the rare-earths interfere with the photometric determination of thorium, it becomes necessary to separate them or to make the necessary correction. We attempted to develop a method for determining this correction; for this purpose use was made of the different relationships between the absorption of the complexes formed by thoron with thorium and the rare-earths and the pH value of the solution. It is clear from the diagram that while the absorption of solutions containing thoron and 10 γ of thorium remain constant on changing the acidity of the solution from 0.005 to 0.14 N, the absorption of solutions containing 2000 γ Ce or La increases with decreasing acidity, within the limits indicated, by 19:1.3 = 14.6 times. Accordingly, by measuring the absorption of solutions containing thorium and cerium (lanthanum) at two different pH's, and knowing how the absorption caused by Ce (La) varied during this change in acidity, it is possible to calculate the value of this absorption, so that an appropriate correction can be applied.

Using such a technique it is possible to determine thorium quantitatively in the presence of an unknown amount of the rare-earths, as long as the character of the relationship between the absorption of the complexes of the individual rare-earths with thoron and the acidity of the solution is the same, independently of the absolute value of the absorption of the individual complexes. Unfortunately, we were only able to study cerium and lanthanum in this connection, Nevertheless, in our opinion, this method could be used for the determination of thorium in the presence of a natural mixture of the rare-earths, since, in the first instance Ce and La account for the bulk of the elements in a natural mixture of the lanthanides, and in the second place one would not expect a sharp difference in the relationship indicated for the remaining rare-earths from that for Ce and La, although, of course, during such a determination a certain indeterminacy always exists. Table 4 contains some results for the determination of thorium in the presence of various amounts of carium by the method indicated.

During the determination of 10γ or more of thorium, the increase over true value caused by the presence of 1-2 mg of the rare-earths can be ignored in practice, if the acidity of the solution being measured photometrically is maintained equal to 0.14 N. In order to get more accurate results a correction should be applied, the value of the correction being ascertained by the method suggested. This method, of course, cannot yield a high accuracy when it is used as a method for separating thorium and the rare-earths, but it may be useful for getting an approximate idea of the increase over the true value caused by these elements during mass analyses.

SUMMARY

Optimum conditions have been established for the photometric determination of thorium by means of thoron when the optical density of the solutions is measured on the FÉK-M photocolorimeter.

A method has been developed for separating microgram amounts of thorium from uranium, iron, and other interfering elements, which is based on coprecipitation of thorium with calcium oxalate from a weakly acid medium.

A method is proposed for the determination of thorium in the presence of cerium and lanthanum; this is based on differences in the absorption of the colored complexes of these elements with thoron at various acidities of the solution. The mean absolute error for the determination of 1-10 γ of thorium is 0.3 γ. The maximum absolute error does not exceed 0.5γ.

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THE ANALYTICAL APPLICATION OF 8-MERCAPTOQUINOLINE (THIOOXINE) AND ITS DERIVATIVES

COMMUNICATION 5. THE PHOTOMETRIC DETERMINATION OF MOLYBDENUM

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The most widely used photometric method for the determination of molybdenum is the thiocyanate method [1,2]. The fairly large instability constant of the thiocyanate complex makes it essential to add a large excess of ammonium thiocyanate, and this leads to the partial formation of the somewhat less intensely colored complex ion $[Mo(SCN)_6]$. During careless reduction of molybdenum to the quinquevalent state there may be formed molybdenum compounds in which the molybdenum is in the lower valence states and these compounds will be less intensely colored. Extracts of molybdenum thiocyanate in organic solvents have low stability. Fe, Co, Ni, Al, Ti, Mn, U, and Ta do not interfere with determination of molybdenum by this method. The platinum metals, silver, gold, and a number of other elements should be absent. This method can be used for the determination of molybdenum in tungsten salts under conditions where iron is absent. Phenylhydrazine [2] and potassium ethylxanthate [3] give a fairly sensitive reaction with molybdenum in acid media.

The phenylhydrazine reaction is used for the determination of molybdenum in ores and silicate rocks [4,5].

In addition to the reagents mentioned above, several sensitive reagents, which, however, are of low specificity have been suggested for determination of molybdenum; these include thioglycollic acid [6], and protocatechaldehyde [7]. Dithiol (4-methyl-1,2-dimercaptobenzene) has started to find use in recent years for the determination of molybdenum in soils and plants. This reagent requires preliminary separation of molybdenum from accompanying elements.

Another drawback of this reagent is its low stability; despite this, because of its high sensitivity, dithiol is finding application for the determination of small amounts of molybdenum (about 0.1 γ) [8-10].

Thiooxine (the sulfur-containing analog of 8-hydroxyquinoline) reacts with molybdates both in weakly and in strongly acid solutions to form insoluble compounds. Depending on the conditions, various molybdenum thiooxinates can be obtained. At pH 2-3, and also in more acid media, ammonium molybdate reacts with thiooxine to form an amorphous brown precipitate, which, in the presence of excess thiooxine becomes green. The green thiooxinate has the composition $MoO_2(C_9H_6NS)_2 \cdot H_2O$.

Found %: Mo 20.64; N 6.29; S 13.67; H_2O 3.82
Calculated %: Mo 20.59; N 6.01; S 13.30; H_2O 3.86

The water of crystallization in the molybdenum complex was determined by two methods: by drying, and by the Chugaev-Zerewitinoff method for the determination of active hydrogen [11]. Both methods gave identical results.

This molybdenum thiooxinate is readily extracted by chloroform, isoamyl alcohol, toluene, xylene, benzene and bromobenzene to give emerald-green colored solutions; it is sparingly soluble in carbon tetrachloride and dichloroethane. It is completely insoluble in aliphatic hydrocarbons. The extracts maintain a constant extinction for at least 24 hours.

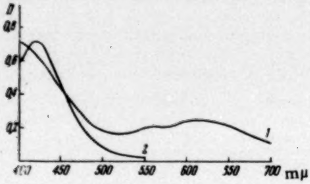

Fig. 1. Absorption curves for molybdenum thiooxinate. 1) Without ascorbic acid; 2) in the presence of ascorbic acid.

At higher acidities thiooxinates of different composition may be formed. In a 1:1 hydrochloric acid solution, there is formed a brown amorphous precipitate containing 16.46 % Mo, 18.14% S, 4.95% N, and 3.54% H_2O. This complex is extracted by chloroform to give a solution with a brown color.

From concentrated hydrochloric acid green crystals are precipitated which contain: 14.80% Mo, 27.14% S, 4.27% N, and 7.29% H_2O.

In weakly acid solutions (pH 3-5), in the presence of ascorbic acid, presumably, there occurs reduction of the molybdenum to the quinquevalent state, since the molybdenum thiooxinate extracted afterwards from 2.3 N HCl has a yellow color. The extractability by organic solvents, and the stability of the extracts of this complex are the same as those for $MoO_2(C_9H_6NS)\cdot H_2O$ mentioned above.

The absorption curves for molybdenum thiooxinates are shown in Fig. 1.

As is evident from Fig. 1, the absorption maximum of the molybdenum thiooxinate extracted by toluene in the presence of ascorbic acid is shifted to long wavelength side of the spectrum, and is found at 420 mμ. The molar extinction coefficient $\epsilon_{420} = 8600$.

All the experiments described below were carried out with the molybdenum thioxinate obtained in the presence of ascorbic acid.

For studying the extractability of the molybdenum thiooxinate as a function of the acidity of the medium, 50 γ of Mo in the form of an aqueous solution (5 ml), and 5 ml of a 10 % ascorbic acid solution were introduced into a separating funnel and left to stand for 2-3 minutes. Then, in the case of high acidities, the calculated amount of hydrochloric acid was added, while in the case of weakly acid solutions a buffer solution with a definite pH was added, until the volume was 50 ml. After addition of 4 ml of 4-5% alcoholic solution of thiooxinedihydrate or thiooxine hydrochloride (in 2.3 N HCl for strongly acid solutions) the molybdenum thiooxinate was extracted with 10 ml of toluene by vigorous shaking for 5 minutes. The extract was filtered through a plug of cotton wool and photometric measurements carried out; the amount of molybdenum was then calculated on the basis of a calibration curve constructed in weakly acid solutions. Since determination of molybdenum in the presence of foreign elements was carried out in a medium of 2.3 N HCl in the presence of oxalic acid (for preventing precipitation of tungstic acid), it was very important to establish the highest acid concentration at which complete extraction of molybdenum thiooxinate could still be carried out. For this purpose 20 ml of a saturated solution of oxalic acid was added to the funnel in addition to the hydrochloric acid. The acidity arising from the presence of the oxalic acid was not taken into account.

As can be seen from Fig. 2, molybdenum thiooxinate can be completely extracted within the limits of pH 5 to 2.3 N HCl; in more acid solutions the extractability of molybdenum thiooxinate gradually drops. In alkaline solutions the molybdate does not react with thiooxine; obviously, under these conditions the molybdate is more stable than the thiooxinate.

Conformation of solutions of the molybdenum complex to Beer's law was studied under the same conditions as those that were use in subsequent work, i. e. in a medium of 2.3N HCl in the presence of ascorbic acid (5 ml of a 10% solution), oxalic acid (20 ml of a saturated solution) and 4 ml of a 5% solution of thiooxine hydrochloride in 2.5 N HCl. The only variable in all the experiments was the amount of molybdenum (from 10 to 250 γ in a volume of 50 ml). As can be seen from Fig. 3, molybdenum thiooxinate solutions conform to Beer's law down to concentrations of 10 γ Mo in 1 ml of toluene. Above this molybdenum concentration there is deviation from linearity; this fact, however, does not preclude the use of this part of the calibration curve for photometric determinations. The method permits the determination of as little as 5γ of Mo in 50 ml of test solution. When an SF-4 spectrophotometer is used and the volume of extract is 5 ml the lower limit is 1.5 γ Mo.

Even very high concentrations of most anions do not interfere with molybdenum determination; thus fluoride, bromide, sulfate, chloride, phosphate, and acetate do not interfere. Several milligrams of thiocyanate in a volume of 50 ml of test solution mask μ gram amounts of molybdenum. Nitrates apparently do not interfere with

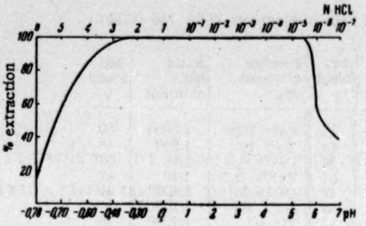

Fig. 2. The relationship between the extractability of molybdenum thiooxinate and the acidity of the solution .

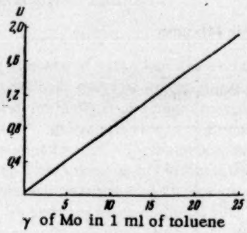

Fig. 3. Conformity of solutions of molybdenum thiooxinate in toluene to Beer's law .

molybdenum determination, but large concentrations of nitrates in a medium of 2.3 N HCl exhibit an oxidizing action on the reagent ; this may be the reason for the low results obtained during determination of molybdenum. Oxalates (20 ml of saturated solution) modify the shape of the calibration curve in the region of high molybdenum concentrations.

Thiooxine, as a reagent which contains the sulfhydryl group, does not react with elements which do not form sulfides which are stable to the action of water. As a consequence of this, high concentrations of the alkali, alkaline-earth metals, Ti, Zr, Cr, Al, etc., do not interfere with molybdenum determination.

The specificity of the thiooxine method depends on the conditions used for carrying out the reaction, and depends in the first instance on the acidity of the medium. In 2.3 N HCl amounts of Fe, Co, Ni, Zn, Cd, Pb, Mn, U, Tl, Ir, Rh which are in considerable excess of the molybdenum have no effect on the accuracy of molybdenum determination. Bi, Ag, Au, Hg, and W under these conditions form thiooxinates which are insoluble in toluene or xylene. The bulky amorphous precipitates of their thiooxinates interfere with the separation of the extract, as a result of which the elements indicated should be masked. Os, Ru, Cu, Pt, and Pd interact with thiooxine in strongly acid solutions and should be masked. Thiourea is used for masking Os, Ru, Pt, Ag, Au, Bi, Hg, and Cu. The thiourea complexes of these elements are readily soluble in water and are more stable than the thiooxinates in the presence of excess thiourea in 2.3 N HCl. Palladium should not be present in amounts greater than 50γ. Tungstic acid is kept in solution by means of oxalic acid. Iron must be reduced to the divalent state with ascorbic acid, while vanadium should be reduced to vanadyl.

Determination of Molybdenum

Preparation of Reagent Solution. 5 g of the potassium salt or the hydrochloride of thiooxine is dissolved in 77 ml of water and 23 ml of concentrated hydrochloric acid (sp. gr. 1.18) added. The clear , orange-yellow solution obtained is stable for several weeks.

Analytical Procedure. To 15-20 ml of a weakly acid (pH 3-5) test solution in a separating funnel is added 4-5 ml of a 8% solution of thiourea and 5 ml of a 10% ascorbic acid solution. The mixture is allowed to stand for 3 minutes and then 10 ml of a sat · oxalic acid solution added, followed by 9.5 ml of concentrated hydrochloric acid (sp. gr. 1.18). Water is added to bring the volume up to 50 ml and the whole thoroughly mixed; 3 ml of reagent solution is then added dropwise and with stirring. Molybdenum thiooxinate is extracted by vigorous shaking with 10 ml of xylene or toluene for 5 minutes. The extract is filtered through a plug of cotton wool and the light absorption of the filtrate determined; the amount of molybdenum is determined on the basis of a calibration curve constructed with the aid of pure solutions of molybdenum, using all the reagents mentioned above. Table 1 contains results for the determination of molybdenum in the presence of foreign elements.

Table 2 contains results for the determination of molybdenum in synthetic mixtures.

SUMMARY

Thiooxine reacts with molybdenum to form an inner-complex salt with the composition $MoO_2(C_9H_6NS)_2 \cdot H_2O$. In the presence of excess thiooxine, the molybdenum complexes are stable in strongly acid solutions and are readily extracted by many organic solvents.

TABLE 1

Determination of Molybdenum in the Presence of Foreign Elements (50 γ Mo taken)

Foreign element, mg	Ratio Mo : element	Mo found, γ	Foreign element, mg	Ratio Mo : element	Mo found γ	Foreign element mg	Ratio Mo : element	Mo found γ
Fe^{2+} 10	1:200	52	Bi^{3+} 25	1:500	51	Cd^{2+} 100	1:2000	50
Ni^{2+} 40	1:800	50	Au^{3+} 25	1:500	48	Zn^{2+} 10	1:200	48
Co^{2+} 5	1:100	50	Sb^{3+}—0,05	1:1	52	Os^{VII} 0,5	1:10	51
W^{VI} 50	1:1000	52	Pt^{IV} 5	1:100	51	Ru^{VIII} 0,5	1:10	47
V^{IV} 50	1:1000	51	Ag^{+} 20	1:400	47	UO^{2+} 50	1:1000	49
Cu^{2+} 5	1:100	52	Pt^{2+} 20	1:400	48	Mn^{2+} 100	1:2000	50
Hg^{2+} 50	1:1000	48	Pd^{2+} 0,05	1:1	52	Tl^{+} 50	1:1000	50

TABLE 2

Determination of Molybdenum in Synthetic Mixtures (50 γ Mo taken)

Foreign elements taken, mg	Mo found, γ	Error, %
Fe^{3+} 10; Ni^{2+} 10; Co^{2+} 10; Mn^{2+} 56	49	−2
Fe^{3+} 10; Ni^{2+} 10; Zn^{2+} 5 Ti^{IV} 10; Z_r^{IV} 20; V^{V} 5	52	+4
Cr^{3+} 20; Mn^{2+} 10; V^{V} 5 Zn^{2+} 5; Cu^{2+} 2; Pb^{2+} 10	51,5	+3
Hg^{2+} 5; Ag^{+} 5; Cu^{2+} 3 Au^{III} 5; Bi^{III} 2	48	−4
W^{VI} 30; Fe^{3+} 5; Cu^{2+} 3 Bi^{III} 2; Ti^{IV} 20; Zr^{IV} 20	52,5	+5

A method has been developed for the determination of molybdenum (1.5-200 γ) in the presence of Fe, Co, Ni, W, V, Cu, Hg, Bi, Au, Pt, Pd, Os, Ru, Pb, Ag, Zn, Cd, U, Tl, and Mn.

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TITRIMETRIC DETERMINATION OF MANGANESE AFTER ITS OXIDATION TO THE TRIVALENT STATE

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The presence of chromium and certain other elements complicates the determination of manganese by titrimetric methods based on oxidation of manganese to permanganate; titration of Mn^{2+} with a solution of a permanganate to MnO_2 is also complicated. This has led to studies of the possibility of using the oxidation of Mn^{2+} to Mn^{III} in the presence of materials forming stable complexes of trivalent manganese, e.g., ethylenediaminetetraacetic acid [1], metaphosphates [2], pyrophosphates [3], and fluorides [4-8]. In these methods it is necessary to filter excess solid oxidizing agent (lead dioxide) [I], to adopt combined oxidation of Mn^{2+} by dichromate in the presence of arsenite [2,4,5], and to resort to the potentiometric determination of the endpoint of the titration of Mn^{2+} with permanganate solution [3,6,7,8],etc ......

The present article contains a description of a simple method of determining Mn^{2+} based on the formation of fluoromanganiate.

Oxidation of Mn^{2+} to "fluoromanganiate" in the presence of excess hydrofluoric acid by the action of potassium nitrate does not proceed quantitatively either in the cold or on heating, as a consequence of the reversibility of the reaction $2Mn^{2+} + NO_3^- + 2nHF \rightleftharpoons 2MnF_n^{(n-3)-} + NO_2^- + (2n-2)H^+ + H_2O$. Actually, on adding excess nitrite to a suspension of $K_2MnF_5 \cdot H_2O$ in hydrofluoric acid, a rapid, complete reduction of the fluoromanganiate occurs. However, ammonium nitrate quantitatively oxidizes Mn^{2+} to fluoromanganiate, since ammonium ions remove nitrite ions ($NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$); excess NO_3^- does not hinder the determination of the fluoromanganiate formed.

Trivalent manganese in the presence of Fe^{III} or Cr^{III} can be determined iodometrically or by titration with Mohr's salt. Results for the determination of Mn^{III} by both methods coincide. Thus, despite the increase in the reducing properties of Fe^{2+} ions in the presence of fluorides, oxidation of Fe^{2+} ions by atmospheric oxygen during the titration does not occur to an appreciable extent; the introduction of boric acid to complex F^- ions, does not affect the results of titration with Mohr's salt. In the presence of chromium it is essential to introduce boric acid before titrating Mn^{III}, since chromium fluoromanganiate $CrF_3 \cdot MnF_3 \cdot 6H_2O$ [9] is very slowly reduced in the presence of excess hydrofluoric acid.

When manganese, iron, and chromium are present simultaneously Mn^{III} cannot be determined iodometrically since Fe^{3+} ions freed from the fluoride complex on addition of boric acid, oxidize the iodide anions.

Moderate amounts of cobalt or nickel salts do not hinder determination of manganese.

Reducing agents (SO_2 and other materials) which are usually present as impurities in hydrofluoric acid do not interfere with the determination, since they are completely oxidized during oxidation of Mn^{2+} to fluoromanganiate.

The concentrations of the standard solutions of chemically pure manganese nitrate, containing 8.47 or 15.56% Mn, were established by the bismuthate method. Aliquots of solutions were taken under conditions which excluded evaporation.

TABLE 1

Oxidation of Mn^{2+} by Nitrates in the Presence of HF

Amount of reagents			°C	Duration of oxidation, minutes	Amount of Mn		Percentage oxidation of Mn, %
40 % HF, ml	KNO_3, g	HN_4NO_3, g			taken, mg	found, mg	
10	1	—	15	30	58,19	26,63	46,08
10	1	—	15	60	43,52	30,02	68,98
10	2	—	15	30	40,87	26,63	65,15
10	1	—	100	30	37,88	28,68	77,48
10	—	2	15	30	49,58	43,80	88,20
10	—	2	100	10	56,26	56,25	99,98
7	—	3	100	10	59,53	59,53	100,00
3	—	1,5	100	10	50,15	49,46	99,62
3	—	0,5	100	10	54,01	46,19	85,30

TABLE 2

Determination of Mn in the Presence of Cr^{3+}

Atomic ratio Cr/Mn in the test solution	Mn taken, mg	Mn found	
		in mg	in %
1	41,11	40,97	99,80
2	36,02	35,85	99,66
4	36,22	36 00	99,40
4	25,28	25,06	99,45
4	26,42	26,36	99,78

TABLE 3

Determination of Mn in the Presence of Fe^{3+} and Cr^{3+}

Atomic ratios in the test solution		Mn taken, mg	Mn found	
Fe/Mn	Cr/Mn		in mg	in %
1	0	21,14	21,03	99,58
4	0	25,63	25,52	99,55
4	2	27,58	27,56	99,94
4	2	29,96	29,60	98,90
4	2	32,20	31,96	99,20
4	2	33,30	33,20	99,80

In the first series of experiments potassium nitrate was the oxidizing agent, while urea was used for combining with the nitrite before titration. It was found (Table 1) that oxidation of Mn^{2+} proceeds with time, increases with increasing temperature, but does not proceed to completion. The use of not less than 1.5 g of NH_4NO_3 and 3 ml of 40% HF permits 1 mg-atom of Mn to be oxidized quantitatively on boiling for 10 minutes on a water bath. The experiments, results of which are given in Table 1, were carried out under the following conditions. To an aliquot of manganese nitrate in a platinum crucible was added hydrofluoric acid and potassium nitrate; the mixture was then kept for a given time at room temperature or on a boiling water bath. After this the mixture was diluted to 100 ml with cold water in a glass flask, and to it was added about 2 g KI, and the iodine liberated titrated with thiosulfate.

Decreasing the initial concentration of the hydrofluoric acid lowers the percentage oxidation of Mn^{2+}; during attempts to use a mixture of nitric acid and 40% hydrofluoric acid as an oxidizing agent, the percentage oxidation of Mn^{2+} dropped rapidly, apparently, because of a decrease in the active concentration of fluoride ions.

Results of the first determinations of manganese in mixtures of Mn^{2+} and Cr^{3+} salts were appreciably low. It was found that the reason for this was not a decrease in the percentage oxidation of Mn^{2+}, but the precipitation of $CrF_3 \cdot MnF_3 \cdot 6H_2O$ which is only slowly reduced by the iodide. Since keeping the solution for a long time before titration with thiosulfate would give rise to the danger of oxidation of I^- by atmospheric oxygen, we tried to accelerate dissolution of the precipitate of $CrF_3 \cdot MnF_3 \cdot 6H_2O$ by addition of boric acid; actually, after adding about 8 g of H_3BO_3 and 50 ml of 10% HCl, the precipitate was rapidly and quantitatively reduced by the iodide.

Under these conditions it is possible to determine the manganese content accurately in the presence of four times its amount of chromium. To aliquots of the solutions placed in a platinum crucible was added 7 ml of 40% HF and 2-3 g of NH_4NO_3; the solution, which was heated for 10 minutes on a boiling water bath, was then transferred into a flask and diluted with a mixture of HCl, H_3BO_3, and water; after addition of KI to this mixture the liberated iodine was titrated with thiosulfate. Results of these determinations are given in Table 2.

TABLE 4

Determination of Mn in the Presence of Co^{2+} or Ni^{2+}

Atomic ratios in the test solution		Mn taken, mg	Mn found		Atomic ratios in the test solution		Mn taken, mg	Mn found	
Co/Mn	Ni/Mn		in mg	in %	Co/Mn	Ni/Mn		in mg	in %
0,9	0	46,10	45,77	99,28	0	0,75	55,59	55,49	99,82
1,0	0	42,64	42,58	99,85	0	0,9	46,31	46,15	99,66
1,8	0	40,57	40,93	100,89	0	1,0	61,40	60,90	99,19
3,6	0	61,24	60,98	99,59	0	1,4	36,11	36,26	100,42
4,0	0	62,20	62,10	99,94	0	2,0	67,80	64,80	95,58
5,0	0	65,45	63,10	96,41	0	3,5	63,22	60,92	96,34
6,7	0	65,86	63,46	96,35	0	6,8	64,49	54,93	85,18

TABLE 5

Determination of Mn in Ferromanganese Containing 74.9% of Mn.

Weight of alloy, mg	Mn, mg	Mn found	
		in mg	in %
34,6	25,92	25,86	99,79
37,0	27,71	27,71	100,00
30,0	22,47	22,70	99,50
34,0	25,46	25,34	99,53
34,8	26,06	25,94	99,52

Mixtures containing Mn^{2+}, Cr^{3+}, and Fe^{3+} were heated with HF and NH_4NO_3 under the same conditions; the mixture was then diluted with 50 ml of 3% NH_4NO_3 containing 8 g H_3BO_3 (partly in suspension) and with water (to a volume of 200 ml); the precipitate of MnO_2 was immediately titrated with a solution of Mohr's salt in the presence of diphenylamine. Results of these determinations are given in Table 3. A further increase in the absolute content of chromium interferes with the determination of manganese, since chromium salts mask the change in color of diphenylamine.

As the results in Table 4 show, the presence of cobalt salts (up to about 250 mg) or nickel salts (up to about 70 mg), does not interfere with the determination of manganese either; under these conditions the determination was finished iodometrically.

It was found that under the conditions used, Co^{2+} salts were not oxidized to Co^{III} as might have been expected on the basis of the extremely strong oxidizing properties of fluorocobaltiates. A drop in the degree of oxidation of Mn^{2+} in the presence of large amounts of Co^{2+} and Ni^{2+} is caused, presumably, by a decrease in the concentration of F^- ions and by the increase in acidity of the solutions caused by oxidation of the fluorides, and also by the dilution of the solutions (Co^{2+} and Ni^{2+} were introduced in the form of the hydrated sulfates).

In conclusion, the applicability of the method developed for the analysis of ferromanganese (standard sample No. 35, containing 74.9% Mn) was checked. An aliquot of the ground ferromanganese, containing about 0.5 g. atom of Mn, was dissolved on heating in 15 ml of 49% HNO_3 contained in a platinum crucible. After the aliquot had dissolved completely, NH_4F in an amount equivalent to the amount of acid taken was added to the crucible; this simultaneously depressed the acidity of the solution (as a result of the replacement of HNO_3 by HF) and introduced the NH_4^+ and F^- ions necessary for the analysis. The mixture was heated for a further 10 minutes and was then transferred into a glass flask by washing with water, after which 50 ml of 3% HNO_3 was added, followed by water (to a volume of about 200 ml); the mixture was immediately titrated with a solution of Mohr's salt in the presence of diphenylamine. As the results given in Table 5 show, the accuracy of the method is fully satisfactory.

SUMMARY

Mn^{2+} ions are quantitatively oxidized to fluoromanganiate on heating them with ammonium nitrate and hydrofluoric acid. Determination of the fluoromanganiate formed can be carried out iodometrically or by titration with Mohr's salt in the presence of diphenylamine.

The presence of salts of Fe^{3+}, Cr^{3+}, Co^{2+}, and Ni^{2+} does not prevent oxidation of the Mn^{2+}.

The slow rate at which the sparingly soluble precipitate $CrF_3 \cdot MnF_3 \cdot 6H_2O$ is reduced by the action of iodide necessitates the addition of boric and hydrochloric acids; when chromium and iron are simultaneously present, the solution should be titrated with Mohr's salt.

The method suggested can be used for analysis of ferromanganese.

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FUNCTIONAL ANALYTICAL GROUPS FOR PALLADIUM

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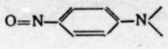
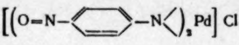
In 1930 Overholzer and Yoe [1] suggested a photometric method of determining Pd (II) by means of p-nitrosodiphenylamine. The same authors investigated a large number of reagents for palladium such as p-nitrosodiphenylamine, p-nitrosoaniline, p-nitrosodimethylaniline, and p-nitrosodiethylaniline [2]. Having studied these reagents and similar compounds, Kul'berg [3] suggested the following functional-analytical group for Pd (II):



According to Overholzer and Yoe's results compounds of the following type are formed:

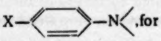


The aims of our investigations were:

a) To find a more general functional group for Pd (II) than that suggested by Kul'berg; b) to develop sensitive photometric methods for determining palladium, including methods for its determination in the presence of platinum.

In this connection we examined 22 organic materials and came to the following conclusions:

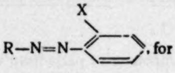
1. The most general group is the following (see Table 1):



, for X $\begin{cases}-NO\\-N{=}N-\end{cases}$

It includes the group found by Kul'berg.

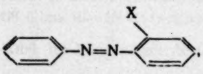
2. During a study of the reactions of palladium (II) with a number of azo dyes (see Table 2) of the type:



, for X = –OH or –COOH

it was found that they all react with palladium.

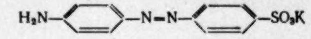
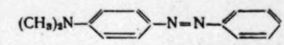
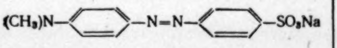
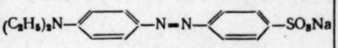
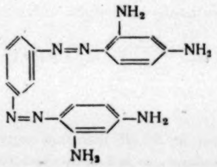
As a result of a comparison of the formulas of the reagents studied it is possible to indicate yet another functional-analytical group with the following structure for palladium:



, for X = –OH or –COOH

For the photometric determination of palladium we chose four reagents, namely: benzyl orange, methyl orange, magneson 1 and methyl red.

TABLE 1

Reagent	Formula	Color of the reagent with:	
		CH_3COONa	CH_3COONa and $PbCl_2$
Benzyl orange		Yellow	Yellow-brown
p-Dimethylaminoazobenzene (dimethyl yellow)		Yellow	Red-brown
Methyl orange		Yellow-orange	Brown
p-Diethylaminoazobenzene-4'-sulfonic acid sodium salt		Orange	Brown
Vesuvin		Orange	Red-brown

The maximum color developed with benzyl orange and methyl orange after 30 minutes.

The color with magneson 1 changed gradually; the optical density of the solutions was always measured after 10 minutes.

The concentration of the $PdCl_2$ solution (established by means of dimethylglyoxime) was 98.33 γ[Pd]/ml. For measurements of the optical density, the reference solution contained the same amounts of the reagents as the solution containing palladium. The pH was maintained constant by addition of sodium acetate (1 ml of a 2 % solution) to the test solution and to the reference solution. The pH used lay outside the color change range when these reagents are used as indicators (6-7.5). The total volume was 10 ml. The optical density was measured on a Pulfrich photometer with a light filter whose transmission maximum coincided approximately with the absorption maximum of the solutions; the pH was determined by means of a pH meter type P_5/P_6 No. 35 .

The results obtained are given in Table 3 and Fig. 1 .

In Fig. 2 are shown the absorption curves of the compounds of palladium with the azo dyes.

Bearing in mind that both components are colored, establishment of the stoichiometric ratios of the reagents during their interaction in solution cannot give conclusive results.

Nevertheless, indications can be obtained regarding the amounts of reagents necessary for developing the optimum color intensity. Both spectrophotometric and refractometric studies of benzyl orange and methyl orange (Tables 4-7) showed that the stoichiometric ratios are, respectively, 6 Pd: 1R and 3 PD: 1R (R = Reagent).

Thus, maximum absorption was obtained with 0.5 ml of reagent for 1 ml $PdCl_2$.

2 ml of 0.01 % benzyl orange was necessary for 393.3 γ Pd.

TABLE 2

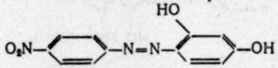
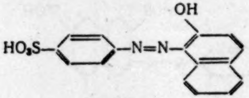
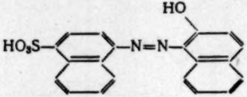
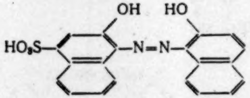
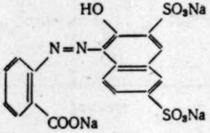
Reagent	Formula	Color of the reagent with: CH_3COONa	Color of the reagent with: CH_3COONa and $PdCl_2$
	A. Monoazo dye		
Magneson I		Yellow-orange	Brown
Orange II		Orange	Red-brown
Red acid A B		Red	Red-violet
Blue acid chromatin		Blue	Red-violet
Alizarin red acid B		Yellow	Orange

TABLE 2 (continuation)

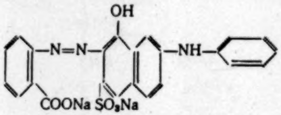
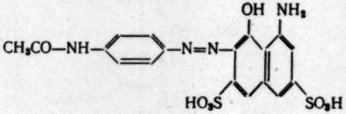
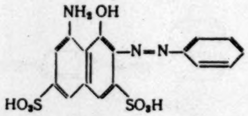
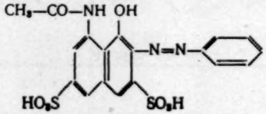
Reagent	Formula	Color of the reagent with:	
		CH_3COONa	CH_3COONa and $PdCl_2$
Anthracene red acid PG		Red-orange	Brown
Azofuchsine 6B		Red	Violet
Red acid 2B		Red	Red-violet
Red acid brilliant G		Red	Intense-red

TABLE 2 (continuation)

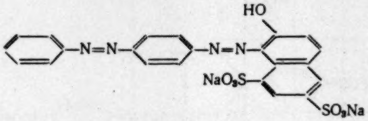
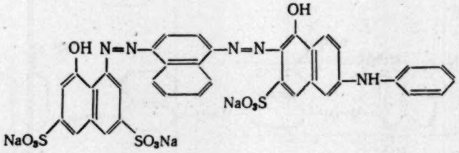
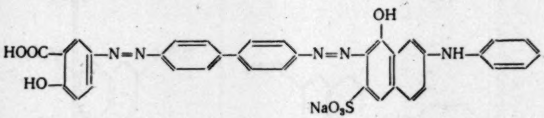
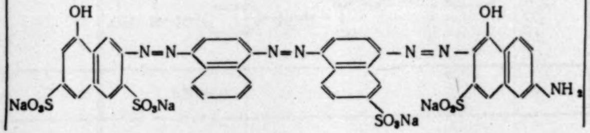
Reagent	Formula	Color of the reagent with:	
		CH_3COONa	CH_3COONa и $PdCl_2$
	B. Diazo- and polyazo dyes		
Puntsovy B. O. extra		Orange	Red
Benz light blue B		Blue	Intense blue
Diamant brown B		Brown	Red-brown
		Blue (light)	Blue

TABLE 2 (continuation)

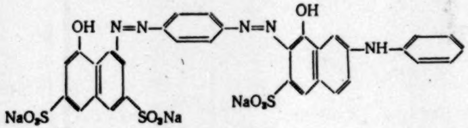
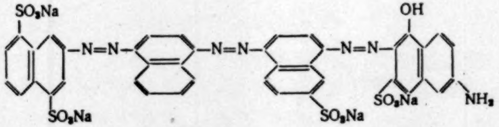
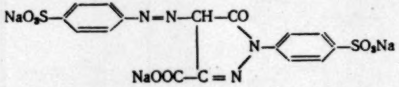
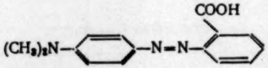
Reagent	Formula	Color of the reagent with :	
		CH_3COONa	CH_3COONa + $PdCl_2$
Benzo light violet B.L.		Violet	Blue
Lilac light blue B 2 R		Blue (light)	Blue
Tartrazine		Yellow	Brown
Methyl red		Yellow-orange	Red-violet

TABLE 3

Pd, γ	Optical density at the absorption maximum, obtained with the reagents:				Notes
	Benzyl orange M_{53}	Methyl orange $M_{[illegible]}$	Magneson I M_{47}	Methyl red M_{47}	
2,5	—	—	—	0,055	2 ml of a 0.01% solution of benzyl orange in ethanol was added
4,9	—	—	—	0,11	2.5 ml of a 0.01% solution of methyl orange in ethanol was added
9,8	—	—	—	0,23	4 ml of a 0.01% solution of magneson in ethanol was added
24,6	0,05	0,075	0,075	0,57	
49,1	0,11	0,15	0,15	1,14	2 ml of 0.01% solution of methyl red in ethanol was added
98,2	0,22	0,30	0,31	—	
196,7	0,44	0,60	0,62	—	(Total volume of solution)
295,0	0,66	0,90	0,93	—	
393,3	0,88	—	—	—	

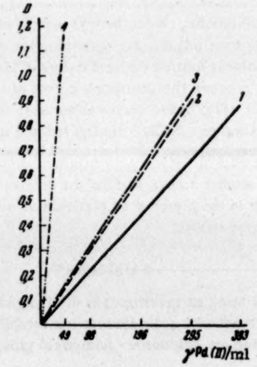


Fig. 1. Conformation of solutions of the compounds of palladium with azo dyes to Beer's law. 1) Benzyl orange. 2) methyl orange; 3) magneson I; 4) methyl red.

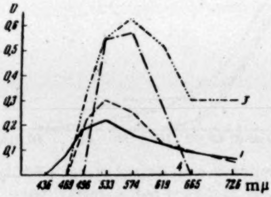


Fig. 2. Absorption curves of the compounds of palladium with azo dyes. 1) Benzyl orange, 98.33 γ Pd; 2) methyl orange, 98.33 γ Pd; 3) magneson 1; 196.66γ; 4) methyl red, 24.58γ Pd.

In order to settle the question of whether the wavelength at which we carried out the determinations was the most suitable (when the absorption of the solutions of reagent is a minimum), we took absorption curves on a

TABLE 4

Stoichiometric Ratio of Pd/ Benzyl Orange (spectrophotometric)

ml $PdCl_2$ 98.33γ/ml	ml of 0.01% reagent	Optical density M_{53}
1	0,1	0,14
1	0,2	0,16
1	0,3	0,16
1	0,4	0,16
1	0,5	0,21
1	5	0,21

TABLE 5

Stoichiometric Ratio of Pd/ Benzyl Orange (refractometric method)

ml $PdCl_2$ 98,33 γ/ ml	ml of 0.01 % reagent	$n_D^{25,5°}$
1	0,1	1,362412
1	0,3	1,362448
1	0,5	1,362484
1	0,8	1,362412
0	Reagent	1,361100

TABLE 6

Stoichiometric Ratio of Pd/ Methyl Orange (spectrophotometric method)

ml $PdCl_2$ 98,33 γ/ ml	ml of 0.01% reagent	Optical density M_{53}
1	0,5	0,19
1	0,75	0,25
1	0,8	0,265
1	0,9	0,295
1	1	0,30

TABLE 7

Stoichiometric Ratio of Pd/ Methyl Orange (refractometric method)

ml $PdCl_2$, 98,33 γ/ ml	ml of 0.01 % reagent	$n_D^{25,5°}$
1	0,5	1,36232
1	0,8	1,36261
1	1	1,36266
1	1,2	1,36259
1	1,5	1,36256
1	2	1,36245
0	Reagent	1,36181
$PdCl_2$	—	1,33257

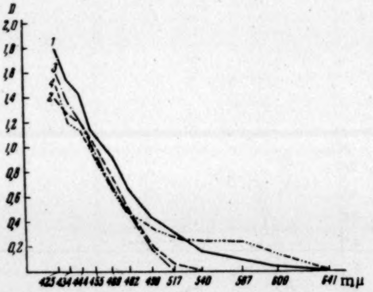


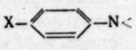
Fig. 3. Absorption curves. Benzyl orange + $PdCl_2$; 2) benzyl orange; 3) methyl red; 4) methyl red + $PdCl_2$.

monochromator. Since benzyl orange and methyl red are the most suitable for determination of palladium (the color is formed immediately and is stable with time) we took the absorption curves of these two compounds (Fig. 3) the curves taken were for benzyl orange, benzyl orange + $PdCl_2$, methyl red and methyl red + $PdCl_2$ respectively.

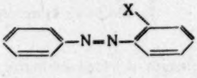
Methyl orange permits the determination of palladium in the presence of platinum at a ratio of 1: 14 with good results.

SUMMARY

During an investigation of 22 organic materials which react with palladium it was established that: the following are functional - analytical groups for Pd^{II}:



where X {—NO, —N=N—



where X {—OH, —COOH

A photometric method of determining from 2.5 to 400 γ of Pd (II) by means of benzyl orange, methyl orange magneson I, and methyl red is suggested.

Methyl red is the most sensitive of the reagents studied; it can be used for the determination of palladium in the presence of 14 times its amount of platinum.

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[3] L. M. Kul'berg, Organic Reagents in Analytical Chemistry, [In Russian], Goskhimizdat (Moscow-Leningrad, 1950).

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RECORDING THE OXYGEN ISOTOPE RATIO IN CARBON MONOXIDE

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Conversion of a MS-2M type mass-spectrometer into a high-precision setup for recording the isotopic ratio of light elements has been dealt with in a previous communication [1]. On a setup of this type research has been carried out on the isotopes of sulfur in natural materials [1-3], and also on oxygen, for paleo-temperature purposes [4,5]. During a study of the isotopic composition of oxygen, both in terrestrial materials and in meteorites, carbon monoxide was used for recording O^{18}/O^{16} [6]. From the viewpoint of mass spectrometry, carbon monoxide has a number of characteristics.

1. Recording of O^{18}/O^{16} is carried out on the basis of masses of 30 ($C^{12}O^{18}$) and 28 ($C^{12}O^{16}$); the latter coincides with the intense background molecular mass (N_2) of the apparatus itself.

2. Mass 28, and, particularly mass 30 are superimposed by fragments of the same masses formed from the hydrocarbons used in the vacuum grease; this considerably complicates recording of the isotopic ratios of oxygen.

3. Carbon monoxide is hardly condensed at all by liquid air so that it is difficult to store it before and after carrying out an analysis.

The present article is devoted to descriptions of

a) constructional details of a receiver for the ions and of a glass attachment to the filling system for the purpose of storing the CO and introducing it into the mass spectrometer during an analysis;

b) a method for recording O^{18}/O^{16} from carbon monoxide for masses of 30 and 28 ;

c) the determination of the absolute ratio of O^{16}/O^{18} for CO adopted earlier as a standard [6].

Ion Receiver and the Construction of a Glass Attachment to the Filling System for Storing CO and for Introducing it into the Mass Spectrometer.

The ratio of O^{18}/O^{16} from carbon monoxide is registered as the ratio of the corresponding masses

$$\frac{30\,[C^{12}O^{18}]}{28\,[C^{12}O^{16}]}.$$

The dispersion of the MS-2M instrument is 1.35 mm for a difference of 1% in the masses, accordingly, in order to realize simultaneousl reception of masses of 30 and 28, the distance between the collector slits should be adjusted to be about 9 mm.

Bearing this fact in mind, a two-collector ion receiver was designed and constructed (Fig. 1), which permitted the distance between the centers of its slits to be changed from 7 to 11 mm.

The fixed slit 3 of the receiver was arranged so that its position coincided with the central beam, while the movable slit 1 was shifted relative to it by a distance which ensured recording of a mass of 28. The slit widths were 1 and 1.5 mm respectively for the fixed and movable slits.

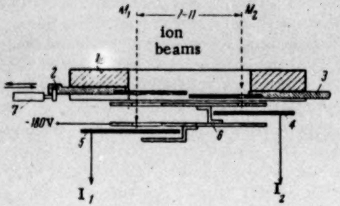

Fig. 1. General appearance of the ion-receiver. 1) Receiver base. 2) movable slit; 3) fixed slit; 4-5) collector plates; 6) suppressing box ; 7) micrometer screw.

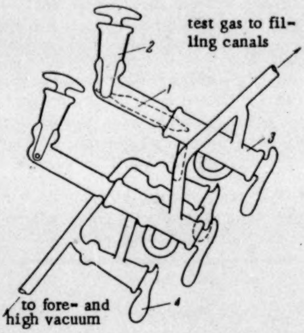

Fig. 2. Glass attachment for the filling system.

In preparing the ion receiver, particular attention was given to screening of the receiver plates 5 and 4 so that secondary electrons did not fall on them. This was achieved by preparing a screened casing 6 (Fig. 1) maintained at a potential of -180 volt.

The receiver plates and the screened casing were made from sheet tantalum 0.3 mm thick, while the rest of the elements of the receiver were made from stainless steel.

Subsequent experimental checks showed that the ion receiver completely fulfilled the purpose it was designed for. In Fig. 2 is shown an attachment — a glass attachment to the filling system — for introducing into the ion source of the mass spectrometer, both the test sample of CO and the CO used as a standard. The ampoules containing the test samples of gas are placed as shown in the diagram in the glass reservoirs. These reservoirs which are fitted with ground joints are connected to the attachment and are pumped out to give a high vacuum; before the test, by rotating the tap 2 the tips of the ampoules are broken and the gas is liberated.

The CO released from each of the ampoules is measured out by taps 3 in turn, and led into the two canals of the filling system, which each is, in turn, passed through the valve system into the mass spectrometer.

After the test gas has been measured out, the gas remaining in the reservoirs can be used for repeated determinations of the isotopic ratios, or its place can be taken by following samples.

When necessary, this attachment can also be used for the analysis of other gases, in particular, nitrogen.

Method for Recording O^{18}/O^{16} from Carbon Monoxide on Masses of 30 and 28.

Comparison of the isotopic ratios of oxygen in test samples and in standard carbon monoxide is linked with a number of difficulties which we shall deal with briefly here, since their resolution will guarantee reliable recording of O^{18}/O^{16}. The masses 30 and 28 which are used for recording the isotopic ratios of oxygen are surrounded by a background. It has proved to be particularly troublesome in the case of mass 30 interference comes from hydrocarbon molecules from the filling system although background value did not exceed 15-17 millivolts. The mass of 30, on switching off the valves, initially slowly increased to 20-21 millivolts, and then even more slowly, in the course of minutes or more, fell to 15-17 millivolts. During recording on a self-recorder, the ratio of the 30/28 masses of the gas samples being compared, as a result of the unstable background, was almost impossible to record. In order to prevent interference from these volatile components which are responsible for the appearance of the background, it was decided to introduce a trap placed in liquid air into the filling canals. The results were contrary to expectations: the ratio of the 30/28 masses was not established, it fell as in the case where was a background of mass 30 present, although the hydrocarbons were prevented from passing into the ion source from the filling canals by freezing out with liquid air. The drop observed, even after taking this precaution, during recording of the ratio 30/28 on the self-recorder ribbon, was related to some separation of the masses on the glass traps cooled to -187°, expressed in the results as an impoverishment in masses of 30($C^{12}O^{18}$) in the test gas passing into the ion source.

On excluding the effect of the background on the isotopic ratio by cooling, a complication connected with separation of the isotopes develops which made things even worse. Recording of the ratios of the oxygen isotopes was possible only by the simultaneous exclusion of the background effect, and prevention of at least an appreciable

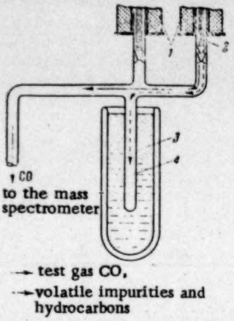

Fig. 3. Attachment for purifying CO from volatile impurities.

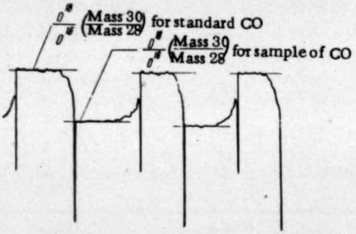

Fig. 4. Recording on the self-recorder ribbon of O^{18}/O^{16} for a sample and for a CO standard.

TABLE 1

Relation between the Nitrogen Content of CO Samples and the Difference in the Isotopic Ratios between the sample and the Standard as a Result of the Nitrogen Present.

Sample No.	Value of mass N^{14} in millivolts for:		Diff. between sample and std., %	Diff. between O^{18}/O^{16} ratios for sample & std., %
	standard	sample		
1	850	1250	47,1	4
2	900	920	2,22	0,2
Dunite 5	900	905	0,55	0,05

separation of the isotopes. If separation of the isotopes can be carried out to the same extent in both the standard and in the sample, no error will be observed. Both these conditions can be fulfilled, as shown experimentally, if immediately after the valves 2 is fitted a glass by pass trap, (see Fig. 2), 4, placed in liquid air 3 (Fig. 3) during analysis of the CO. Hydrocarbon and other volatile components are condensed in the cooled trap, while the test gas (carbon monoxide) which hardly separates at all, passes into the ion source of the apparatus. By introducing such an attachment, the background to the operating masses of 30 and 28 was depressed to 5-6 millivolts and remained stable on switching over the valves. In Fig. 4 is shown a recording of the isotopic ratios of oxygen for a sample and for a standard, which shows that the unstable effect of the background has been eliminated, and, even after switching over the valves, the preceding gas is rapidly replaced by the next sample, while O^{18}/O^{16} comes out as a straight line. The distance between the ratios for the sample and the standard is the difference sought expressed as a percentage.

Masses of 28 and 30 belonging to carbon monoxide, coincide during recording with molecular nitrogen, accordingly, during analysis, one must bear in mind the possibility of contamination of a test sample of CO by atmospheric nitrogen, when a sufficiently high vacuum is not obtained.

The presence of nitrogen as an impurity in test CO means that the recorded ratio of the masses 30/28 is "facilitated" because of the preferential superposition of N^{14}-N^{14} on the 28 mass, which is readily understable knowing the distribution of nitrogen atoms in nature [7].

Control of the presence of nitrogen in CO samples was carried out by comparing the atomic mass 14 (N^+) for a standard and for the sample. In the absence of nitrogen as an impurity in the gases being compared, the intensity of mass 14 will be the same, while in its presence (in CO samples for example), the peak for mass 14 for a sample will be higher than that for the standard in the case of levelled intensities of mass 28.

Table 1 contains as examples some results obtained for a number of samples containing various amounts of nitrogen as impurity.

As can be seen from Table 1, there exists some correlation between the amount of nitrogen present as an impurity in a sample as compared with that in standard, and the difference obtained between O^{18}/O^{16} for the standard and the sample as a result of the presence of this nitrogen.

It was found experimentally that control of CO samples on the basis of the atomic nitrogen mass guarantees the test gas to be free from contamination by nitrogen within the limits up to 0.5%, which means an error in the difference between the O^{18}/O^{16} ratios of 0.05% (Dunite 5). In the same way it is possible to control test samples of CO contaminated by nitrogen on the basis of mass C^{12}.

In order to get results as close as possible to the actual values, samples of CO were prepared independently

TABLE 2

Reproducibility of the Results of Isotopic Analysis of Oxygen for CO Samples Prepared at Different Times

Sample	Difference of the O^{18}/O^{16} ratio for sample and standard, %
"Zhovtnev Hamlet" meteorite	—0,72; —0,70
"Pallasov Iron" meteorite	—0,74; —0,74
"Saratov" meteorite	—0,75; —0,72
Dunite 5	—0,60; —0,55
Dunite 6	—0,73; —0,76
Stannern meteorite (akhondrite)	—0,80; —0,78; —0,78
Quartz, Neroik deposit, Urals	0,00; 0,00; 0,00; 0,00

twice, and sometimes three times, and were measured at different times. The agreement between the results enabled us to conclude that the isotopic ratio for oxygen for a given sample was established correctly.

Table 2 contains results for a number of independent measurements of CO samples prepared at different times.

It is clear from Table 2 that the recorded results lie within the limits of 0.02%, except in Dunite 6 where this difference amounts to 0.05% because of contamination by nitrogen, as is evident from Table 1.

In conclusion we should point out that during recording of the ratio $\frac{30\,[C^{12}O^{18}]}{28\,[C^{12}O^{16}]}$ the preamplifier resistances were fixed at 5×10^{11} ohms for a mass of 30 and at 5×10^{10} ohms for a mass of 28.

Determination of the Absolute Ratio O^{16}/O^{18} for CO Accepted as a Standard.

Nier [8] has established the absolute distribution of the isotopes of atmospheric oxygen. Results of the measurements of the isotopic ratios of oxygen from various materials, carried out by various authors, were obtained relative to standards arbitrarily chosen by these authors, the absolute ratio O^{16}/O^{18} for these standards being unknown. This fact lowers the value of these investigations considerably, since it is impossible to compare the various results. We have tried to fill this gap; for this purpose, in addition to recording the difference between the isotopic ratios of the standard and the samples, expressed in percentage, we also obtained the absolute ratio O^{16}/O^{18} for each of the samples of CO measured.

We found a method which permits a fairly accurate determination (± 0.2 %) of the ratio O^{16}/O^{18} from carbon monoxide, using S^{32}/S^{34} obtained from SO_2 as a standard. The SO_2 was prepared by ignition of troilite (iron meteorite) for which $S^{32}/S^{34} = 22.200$, this being the same for all meteorites (stone and iron) [3]. S^{32}/S^{34} as a standard for comparing O^{16}/O^{18} was chosen for the reason that its isotopic ratio is known, and therefore by using it is is possible to exclude the discrimination of the apparatus. In addition, measurement of O^{16}/O^{18} is a very difficult problem because of the small distribution of O^{18}(0.204%). Actually, in order to obtain an intensity of several hundred millivolts for a mass of 30, the intensity of mass 28 should be expressed in hundreds of volts. Such an increase in the more widely distributed mass would lead to its deformation during recording from Coulomb interactions between the ions, leading to diffusion of the peak, discharge of ions in the receiver, and nonlinearity of the preamplifier, etc.

All this complicates accurate recording of O^{16}/O^{18}. If, therefore CO and SO_2 are introduced into the mass-spectrometer through the two canals of the filling system, and the intensities of the most widely distributed masses of oxygen and sulfur are levelled and they are excluded from all discrimination, then it should be possible, by comparing the least widely distributed masses, to determine O^{16}/O^{18}.

Let us consider the equations

$$S^{32}/S^{34} = 22.200 \qquad (1)$$

and

$$O^{16}/O^{18} = X \qquad (2)$$

TABLE 3

Results Obtained during Determination of the Absolute Ratio O^{16}/O^{18} for CO used as a Standard in [6]

Peak for mass 30 minus back-ground	Peak for mass 30 minus the contribution $C^{13}O^{17}$	Peak for mass 50 minus back-ground	Peak for mass 50 minus the contribution $S^{32}O^{18}$	$\frac{O^{16}}{O^{18}}$
416	415	9560	9102	486,8
536	535	12100	11544	486,4
414	413	9530	9092	488,6

By equating the intensity of S^{32} to O^{16} and excluding them from equations (1) and (2) then

$$O^{16}/O^{18} = X = 22.200.\ S^{34}/O^{18} \qquad (3)$$

but

$$\frac{S^{32}}{S^{34}} = \frac{48\,[S^{32}O^{16}]}{50\,[S^{34}O^{16}]}. \qquad (4)$$

Mass 50 is made up from $S^{34}O^{16} + S^{32}O^{18}$; accordingly, in order to get equation (4), it is necessary to substract 4.6 %, as the contribution of $S^{32}O^{18}$, from the recorded intensity for the peak of mass 50

and

$$\frac{O^{16}}{O^{18}} = \frac{28\,[C^{12}O^{16}]}{30\,[C^{12}O^{18}]}. \qquad (5)$$

Mass 30 is made up from $C^{12}O^{18} + C^{13}O^{17}$, accordingly, in order to get equation (5) it is necessary to subtract 0.2%, as the contribution of $C^{13}O^{17}$ from the recorded intensity of the peak for mass 30.

The experiment is carried out as follows.

Mass 30 is made up from $C^{12}O^{18} + C^{13}O^{17}$; accordingly, in order to get equation (5) we substract 0.2% from the recorded intensity of the peak for mass 30. The experiment is carried out as follows.

An M-193 voltmeter with a well-calibrated scale is connected to the output of the amplifier recording the less widely distributed masses O^{18} and S^{34}. CO is introduced into one of the filling canals and peak values are recorded simultaneously on both amplifiers — mass 30 on one, 28 on the other. SO_2 is then introduced into the second canal and masses of 50 and 48 are recorded, as in the case of the CO, on the two amplifiers. SO_2 is introduced so that the intensity of mass 48 ($S^{32}O^{16}$) is equal to that of mass 28 ($C^{12}O^{16}$).

From intensities for peaks 30 and 50 we get the ratio S^{34}/O^{18}, by deducting the background present before introduction of the gases being compared, and introducing a correction for $C^{13}O^{17}$ and $S^{32}O^{18}$, as indicated above.

Results of these measurements are given in Table 3. From them it is possible to conclude that O^{16}/O^{18} for the standard used in [6] is 487 ± 1.

SUMMARY

A design for an ion receiver capable of simultaneously recording masses of 28 and 30 is described, as well as a glass attachment for the filling system which sotres the CO to be analyzed and fills the mass spectrometer. A method is suggested for precise recording of the oxygen isotope ratio in CO, and a method is described for determining the absolute ratio O^{16}/O^{18} based on using $S^{32}/S^{34} = 22.200$ from the troilite of an iron meteorite as a standard.

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POLAROGRAPHIC DETERMINATION OF SMALL AMOUNTS OF PHENOL ON A ROTATING PLATINUM ANODE

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In recent years solid electrodes have found increasing use in polarographic analysis and for studying the kinetics of electrochemical processes [1-10].

Because of certain peculiarities of the dropping-mercury electrode, the application of solid electrodes has acquired special significance for the polarographic study and analysis of those classes of organic compounds, which are either subject to direct oxidation, or are strong oxidizing agents. Nevertheless, the practical application of solid anodes for the polarographic determination of organic compounds has come up agains a number of serious difficulties connected with the characteristics of diffusion kinetics and with specific changes in the state of the surface of the solid electrode during the process of anodic polarization. It is for this reason that this interesting problem is represented in the literature by only a few papers [1-6], while the results of these papers do not satisfy the requirements of reproducibility and accuracy of quantitative polarographic analysis.

The work described here is devoted to the polarographic determination of small amounts of phenol on a rotating platinum anode.

Experimental Technique. The following reagents were used; 1) phenol, "pure" and chemically pure grades $d_{45} = 1.0550$, $n_D^{45} = 1.5400$; 2) highly pure phenol subjected to a two-fold distillation ($d_{45} = 1.0545$; $n_D^{45} = 1.5391$); 3) production fraction — "phenol water".

The supporting electrolyte had the following composition: 0.1 M $NaNO_3$ + 0.1M H_3BO_3 + NaOH; pH 10.7 (± 0.1).

A 1.0×10^{-3}M aqueous solution of phenol served as the original standard solution for preparing samples.

Polarographic determination of phenol was carried out on a cylindrical, rotating platinum anode the solution being kept at a constant temperature. A platinum wire 0.5-1.5 mm in diameter and 10-12 mm long was fused into a brass rod which was fitted onto the motor shaft by means of a holder. The current was fed to the electrode by means of a special attachment fitted to the motor axle. The speed of the motor was regulated and the number of revolutions of the electrode (the motor axle) kept constant by means of an autotransformer connected to a ferroresonance voltage stabilizer. For keeping the working surface of the electrode constant, a glass bead was fused on the electrode at a distance of 5-7 mm from its tip; this served as a marker for the depth to which the electrode was immersed in the solution.

The open electrolytic cell had two sections separated by a thin plug of agar-agar. One of the sections was filled with the test solution in which the platinum anode was immersed, while the other section formed the saturated calomel half-element. The resistance of such an electrolytic cell was 700-900 ohms.

Experimental Results. In an earlier paper [11] devoted to the oxidation of phenol on a platinum anode, it was established that, on the one hand, the shape and height of the phenol diffusion wave, and also the reproducibility of successive polarograms, depend to a considerable extent on the nature of the preliminary treatment of the platinum anode, while on the other hand during the time that one polarogram is being characteristic taken "poisoning" of the electrode occurs. This poisoning was manifested by the deposition of a scarcely observable dark-brown deposit of phenol oxidation products on the electrode surface, while the diffusion current, and, accordingly, the sensitivity of the electrode with respect to the current, dropped sharply from experiment to experiment. Attempts to eliminate "poisoning" of the electrode completely by chemical treatment of the electrode surface with various organic solvents, aqua regia, hot alkali solutions, and sulfuric acid were not successful. Electrochemical treatment of the electrode was not sufficiently effective either for this purpose.

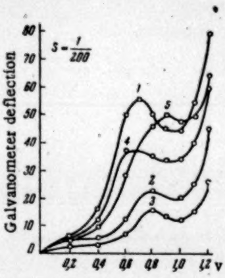

Fig. 1. Effect of the conditions used for treating the electrode on the shape of successive polarographic waves;phenol concentration 0.65 x 10^{-4} M ; polarization rate 2.6 millivolts/ second. 1) Electrode annealed for 2-3 seconds; 2) without annealing; 3) without annealing; 4) electrode annealted for 2-3 seconds; 5) coating removed and electrode annealed for 2-3 seconds,

It is clear from Fig. 1 that on all the polarograms taken in succession, in a solution containing a constant concentration of phenol, (0.65 x 10^{-6}M), "poisoning" of the electrode is characterized by a drop in the diffusion currents (Curves 1, 2, 3) and by the appearance of typical maxima on the polarograms.

A preliminary, short-duration (2-3 seconds) annealing of the electrode in the oxidizing flame of a gas burner only partially eliminated subsequent poisoning of the electrode (Curve 4). When the deposit was removed (by means of ashless filter paper) and the electrode annealed, in succession, a diffusion effect was observed (Curve 5).

From the results of this preliminary work it became clear that in order to develop a quantitative polarographic technique of analysis, it is of primary importance to establish the conditions for preparing the electrode which will ensure a reproducible and standard state of its surface, and also to find a method of preventing or eliminating "poisoning" of the electrode during the time when one polarogram is being taken, and during the taking of a succession of polarograms.

This problem was experimentally solved in two variants. The first variant for preparing the platinum electrode consisted of the following operations:

1) a smooth platinum electrode was treated for 5 seconds in concentrated nitric acid; 2) it was then washed tith distilled water; 3) the electrode was subjected to a three-fold stepwise anodic polarization over the range 0.0-1.5 volt. An electrode subjected once to such treatment could be kept for a long time (up to one month) in a working condition without additional preparation. After each polarogram had been taken, the brown deposit of phenol oxidation products was removed (with ashless filter paper), and the electrode annealed for a short time (about 2 seconds) in the oxidizing flame of a gas burner.

Before taking each polarogram the potential of the platinum anode was restored to the original standard value by short-circuiting to the calomel electrode.

In the second, simplified variant, anodic polarization was omitted, while the electrode was annealed for a longer time (5-6 seconds)until it was red hot. It was established that the use of either anodic treatment, or annealing of the electrode, was a necessary condition for obtaining low residual currents and a clearly defined phenol wave corresponding to a high limiting current. On the other hand, it was shown that annealing the electrode for 5 seconds not only replaces the action of anodic treatment, but, in addition, simultaneously eliminates the results of the "poisoning" of the electrode.

As a result of a study of the relationship between a number of polarographic characteristics and such factors as the state of the anode surface, the speed of rotation of the anode, the polarization rate (potential change), phenol concentration, and solution temperature, optimum conditions were found [11] for taking polarograms which were applicable to the quantitative analysis of small amounts of phenol in aqueous solutions.

The results given in the rest of this article were obtained on rotating platinum anodes rotating at a stable speed greater than 1200 revolutions/ minute, and at a polarization rate of 5.0-8.0 millivolts/ second.

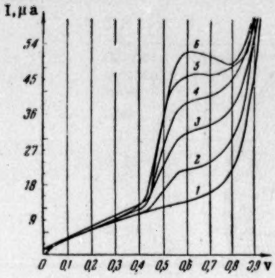

Fig. 2. Polarograms for phenol on a rotating platinum electrode. 1) Buffered supporting electrolyte; 2) phenol concentrations: 2×10^{-5}M; 3) 4×10^{-5}M; 4) 6×10^{-5}M; 5) 8.0×10^{-5}M; 6) 1.0×10^{-4}M; polarization rate 8.3 millivolts/second; t = 24°.

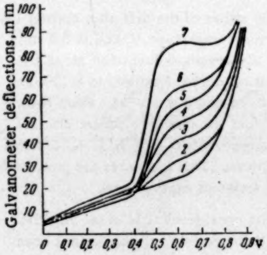

Fig. 3. Polarograms for phenol on a rotating platinum anode. 1) Buffered supporting electrolyte 0.1 M; 2) phenol concentrations: 2×10^{-5} M; 3) 4×10^{-5}M; 4) 6×10^{-5} M; 5) 8×10^{-5}M; 6) 1.0×10^{-4}M; 7) 1.5×10^{-4}M. Polarization rate 6.2 millivolts / second; t = 24°.

All potentials are referred to the saturated calomel electrode.

In Fig. 2 and 3 are shown typical series of photopolarograms for aqueous solutions of phenol within the concentration limits $1.0 \times 10^{-5} - 1.0 \times 10^{-4}$M and $1.0 \times 10^{-5} - 1.5 \times 10^{-4}$M, taken on various automatic polarographs, when two different platinum anodes were used. Readily reproducible results were obtained for each series of experiments. Fig. 4 illustrates polarograms taken on a disc diagram for $1.0 \times 10^{-5} - 1.0 \times 10^{-4}$ M phenol solutions; these were taken on an indicating and recording electron polargraph of special construction, developed in the Scientific Research Institute of Synthetic Alcohols by V. I. Ginzburg and L. S. Klyainshtein.

In Fig. 5 is shown the relation between the limiting current and concentration for the series of polarograms in Fig. 3.

As is evident from Fig. 2, 3, 4 and 5, under the given conditions there are observed clearly defined diffusion waves corresponding to large limiting currents. Under these conditions, within the concentration range $1.0 \times 10^{-5} - 1.0 \times 10^{-4}$M, there is observed a linear relationship between the limiting current and concentration. Further increases in the concentration above $1.0 - 1.25 \times 10^{-4}$M lead to the appearance of maxima to a and gradual increase of the maxima on the curves, this being accompanied by a breakdown in the linear function $i_d - C$. Thus, from Figs. 3 and 5 it can be seen that at a concentration of 1.5×10^{-4}M there is an obvious maximum, while the value of the limiting current is somewhat less than that which corresponds to a strict linear relationship of the function $i_d - C$, the point on Fig. 5 is arranged slightly below the straigt line.

The experimental results indicate that it is possible, in principle, to carry out a quantitative polarographic determination of small amounts of phenol in aqueous solutions.

In order to evaluate the practical expediency of the wide use of this method for analytical purposes, we determined its accuracy by means of synthetic mixtures and production samples of phenol-containing solutions.

In Table 1 and Fig. 6 are given the results of one typical series of experiments which give an idea of the reporducibility and accuracy of the suggested polarographic method. For each sample with a known phenol concentration (wave-height $d_{45} = 1.0545$; $n_D^{45} = 1.5391$) four polarograms were taken in succession. In columns 2, 3, and 4 of Table 1 are listed the value of the limiting current (i_d), the arithmetic mean for the limiting current (i_d mean), and mean-square error of a single result (F_m^{id}). The last value characterizes the reproducibility of measurements based on the limiting current. As is evident from Fig. 6, the relation between the limiting diffusion current and concentration (according to the results of Columns 1 and 2 of Table 1) is linear. By means of the calibration curve, Fig. 6, the values of the mean square error of a single result for each concentration (F_m^c) was calculated, as well as the mean square error of a single result for all the concentration range (F_m^{id-c}), and the probable mean-square error for a series of measurements (U_m^{id-c}). From comparison of the values given in Columns 4 and 5 of Table 1 it can be concluded that the mean-square errors calculated on the basis of the limiting current or concentration are identical. Consequently, it can be affirmed that for polarographic methods of study based on comparison of test solutions with standard solutions (taken as a criterion of the true values), the reproducibility based on the limiting current serves as a condition sufficient for characterizing the accuracy of the method.

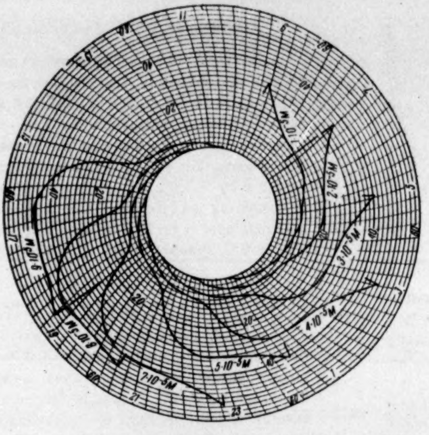

Fig. 4. Polarograms for phenol on a rotating platinum anode, taken on an electron polarograph.

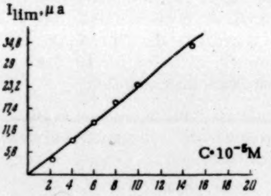

Fig. 5. Relation between the limiting diffusion current and phenol concentration when a rotating platinum anode is used. Polarization rate 6.2 millivolts/second.

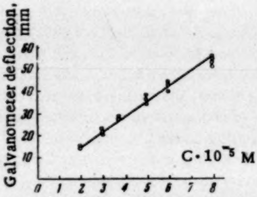

Fig. 6. Calibration curve for determination of phenol on a rotating platinum anode.

The accuracy with which the value of the diffusion current can be read visually on a Heyrovsky polarograph, type V-ÉOI, is 0.5 mm, which, calculated in terms of the mean-square deviation along the abscissa on the basis of the calibration curve, amounts to 3.13% and 0.78% for concentrations of 2×10^{-5}M and 8×10^{-5}M. From the results given in Table 1 it follows that the probable square error of the mean value of a series of measurements is 0.35%, i. e., it is less than the value of the square deviations. This indicates the permissible limits of random errors in a given series of experiments.

From the experimental results considered it is clear that the mean square error of a single result for various concentrations does not exceed 3.5%, while the mean-square error of a single result for all the concentration range (which characterizes the accuracy of the given method) amounts to 2.5%.

For practical purposes it was of interest to apply the present method for the direct polarographic determination of phenol in colored and turbid production media and in tap water containing other organic materials as impurities.

As test material for evaluating the practical applicability of the given polarographic method a production fraction "phenol water" was used; this fraction had, depending on technical conditions, the following composition (in % weight): phenol 4-5.5%; acetone 0.1-0.3 %; α-methyl styrene 0.8-0.1 %; acetophenone 0.5-1.0%; and H_2O 92-93 %.

As a result of carrying out a series of comparative polarographic measurements for solutions containing only phenol, and phenol plus small additions of α-methyl styrene, acetophenone, and acetone, it was established that the presence of the impurities indicated in solution does not affect the value of the limiting diffusion current, and, consequently, will not hinder the direct polarographic analysis of phenol in such production fractions.

TABLE 1

Phenol concen. mole/liter	i_d, mm	Arithmetic error, i_d, mm	Mean-square error $F_m^{i_d}$, %	Mean-square error F_m^{c}, %	Phenol concen. mole/liter	i_d, mm	Arithmetic error, i_d, mm	Mean-square error $F_m^{i_d}$, %	Mean-square error F_m^{c}, %
$2 \cdot 10^{-5}$	14	14,12	1,77	1,91	$5 \cdot 10^{-5}$	35,5	35,5	3,04	3,51
	14,5					37,0			
	14					34,5			
	14					35,0			
$3 \cdot 10^{-5}$	20,5	21,0	1,94	2,06	$6 \cdot 10^{-5}$	43,0	42,25	2,81	3,04
	21,0					40,5			
	21,0					43,0			
	21,5					42,5			
$4 \cdot 10^{-5}$	28,0	27,62	2,71	3,44	$8 \cdot 10^{-5}$	55,0	54,5	1,67	2,78
	28,0					54,0			
	28,0					53,0			
	26,5					55,5			

$f_m^{i_d-c}$ — Mean arithmetic error single measurement = 1,90%; $F_m^{i_d-c} =$

$= \sqrt{\frac{\Sigma f^2}{n-1}}$ — Mean-square error single measurement =2,53%; $U_m^{i_d-c} =$

$= \frac{F_m^{i_d-c}}{0,67\sqrt{n}}$ — Probable square error of mean value of a series of measurements= 0.35%

= ,35%.

TABLE 2

% of phenol in phenol water	Deviation from the mean value	% of phenol in phenol water	Deviation from the mean value	% of phenol in phenol water	Deviation from the mean value
5,26	+2,5	5,38	+ 4,9	4,87	—5,1
5,57	+8,6	5,41	+ 5,4	5,32	+3,7
4,94	—3,7	5,10	— 0,6	5,01	—2,3
4.95	—3,5	5,17	+ 0,8	4,90	—4,5
5,04	—1,7	4,60	—10,0	5,45	+6,2
5,13	0,0	5,25	+ 2,3	5,07	—1,2

Note. The mean phenol content is 5.13% ; f_m = 3.3% ; Fm = 4.7 %.

Table 2 contains the results of repeated polarographic determinations of phenol in the same production fraction ("phenol water"); these determinations were carried out by two workers on different platinum anodes and different polarographs. The phenol content of the test solution was determined by the comparison method. Dilution of samples to be analyzed polarographically was carried so that their phenol content was within the range 1.0×10^{-5} to 1.0×10^{-4}M. A 1.0×10^{-3}M solution of high-grade phenol was used for preparing the standard solutions.

The phenol content of the original test solution ("phenol water") was calculated by means of the formula

$$X = \frac{h_2 \cdot c \cdot b \cdot 9{,}41}{h_1},$$

where h_1 is the limiting (maximum) diffusion current of the standard sample in mm of the galvanometer scale or in μa; h_2 is corresponding value for the test solution; c is the molar concentration of the standard solution; v is the dilution of the test solution.

It follows from the results given in Table 2 that the arithmetic mean-square error of a single determination, which characterize the accuracy of the polarographic method of analyzing phenol in "phenol water", are 3.3 and 4.7 % respectively.

It should be noted that the evaluation of the accuracy of the analytical method for determining phenol in production fractions, was deliberately carried out under the most severe conditions corresponding to the maximum possible systematic and random errors of a given series of measurements.

The experimental results obtained allow one to conclude that the accuracy of the recommended polarographic method is high enough and completely satisfies the requirements of series analysis of phenol in production fractions. It would be expedient to make wide use of such a polarographic method for the analysis of phenol, in view of its advantages over other chemical and physicochemical methods of analyzing phenol.

The method permits comparatively rapid, fairly accurate, determinations of small amounts of phenol (down to 1.0×10^{-5} M) directly in colored, turbid media, containing impurities in the form of other organic materials, in particular α-methyl styrene, acetophenone, and acetone.

SUMMARY

Optimum conditions have been established for preparing rotating platinum anodes, so that clearly defined and reproducible polarographic waves are obtained for phenol, corresponding to large limiting currents.

A new method has been developed for the polarographic determination of small amounts of phenol using a rotating platinum anode. The method can be used for the direct determination of small amounts of phenol (down to 1.0×10^{-5} M) directly in the colored, turbid media containing other organic materials present as impurities and, in particular α-methyl styrene, acetophenone, and acetone. The mean-square error of the method is 2.5-4.7 %.

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ANALYSIS OF NITROPARAFFINS BY PARTITION CHROMATOGRAPHY

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Determination of individual nitroparaffins in their mixtures is one of the very difficult problems of analytical chemistry. Methods based on reduction of the nitroparaffins only permits determination of their sum [1-9]. The same is almost true of polarographic methods [3-7]. Methods based on differences in the behavior of primary, secondary, and tertiary nitroparaffins toward alkalis only permit the possibility of group analysis [1,8]. A rapid method of determining nitroparaffins based on their chlorination [9], according to the authors themselves, can only be applied for the determination of functional groups and then only in the absence of compounds which can be oxidized or chlorinated. Wider possibilities are opened up by the photometric method [10-16], but even this does not ensure complete analysis of a mixture, even of the simplest nitroparaffins (C_1-C_3). In a number of cases only total nitroparaffins can be determined by this method. Of the individual nitroparaffins, 2-nitropropane [10] and nitromethane [11,14,16] can be determined with reasonable confidence. When nitroethane and 1-nitropropane are present simultaneously only their sum can be determined [11,13].

A mass-spectrometric method described recently [17] requires complicated equipment. The relative closeness of the boiling points of the nitroparaffins complicates their analysis by fractionation also.

We tried to use partition chromatography for separating a mixture of the simplest nitroparaffins (C_1-C_3). The nitroparaffins were reduced to the corresponding amines, the mixture of which was then separated chromatographically. The reduction rate of the simplest nitroparaffins is approximately the same (Table 1).

Thus, the percentage proportion of the amines obtained, does not differ in practice from the proportions of the nitroparaffins in the mixture prior to reduction. Knowing the total alkylamine content and the amount of each of the alkylamines, it is possible to determine the percentage composition of the nitroparaffins.

The total content of alkylamines is readily determined by titrating a mixture of their salts with alkali in an aqueous acetone medium, a small amount of formalin being added toward the end of titration [18]. The individual alkylamines in the mixture obtained can be separated by partition chromatography. The application of this method for separating mixtures of primary, secondary, and tertiary alkylamines with carbon chains of the same length, has been described in the literature [19-21]. The same principle, with some modifications to the analytical method, can be used also for separating mixtures of primary alkylamines with carbon chains of different length.

EXPERIMENTAL PROCEDURE

Any method which permits nitroparaffins to be reduced to the amines at the same rate can be used for reducing the nitroparaffins. We used the method of Johnson and Degering [22], and established that by using sufficiently active reduced iron, the process is completed considerably more rapidly than the authors indicated.

The amines obtained, after the reaction solution has been made alkaline, were distilled into 0.5 N sulfuric acid. The solution was evaporated to 10 ml. 1 ml of the solution obtained was placed in a 250 ml flask. Free sulfuric acid was neutralized with 0.1 N NaOH. The amount of the latter required was determined beforehand by titration of a separate aliquot with alkali using methyl red as indicator. To the neutralized solution was added 35 ml of acetone neutralized with respect to phenolphthalein and the mixture titrated with 0.1 N NaOH until a pale-rose color was obtained. 5 ml of formalin neutralized with respect to phenolphthalein was then added after which the solution was again titrated to a pale rose color; the amount of alkali used corresponds to the total content of alkylamines in the test solution.

TABLE 1

Yield of Amines During Reduction of Various Nitroparaffins by Iron and Hydrochloric Acid

Nitroparaffin	Taken, g	Iron used up for the reduction, g	Reduction time (hours)	Yield of amine, %
Nitromethane	0,5	30	6	100,7
Nitroethane	0,5	30	6	97,0
1-Nitropropane	0,5	30	6	97,6
2-Nitropropane	0,5	30	6	100,7
Nitromethane	1.0	10	4	91,4
Nitroethane	1,0	10	4	93,7
1-Nitropropane	1,0	10	4	94,2
2-Nitropropane	1,0	10	4	94,1

TABLE 2

Separation of Mixtures of the Salts of Primary Alkylamines Obtained by the Reduction of the Corresponding Nitroparaffins

Mixture No.	Comp. of orig. mix.		Nitroparaffins found		Relative error
	Components	%	0.05 N HCl used, ml	amount, % %	
1	1-Nitropropane	55,9	12,6	53,0	—5,2
	Nitroethane	44,1	11,2	47,0	+6,5
2	1-Nitropropane	43,4	10,9	42,2	—2,7
	Nitroethane	56,6	14.9	57,8	+1,1
3	1-Nitropropane	49,9	8,6	46,5	—6,8
	Nitroethane	42,6	8,5	45,9	+7,7
	Nitromethane	7,5	1,4	7,6	+1,3
4	2-Nitropropane				
	1-Nitropropane	47,9	13,0	45,0	—6,0
	Nitroethane	43,4	13,2	45,7	+5,3
	Nitromethane	8,7	2,7	9,3	+7,5

Chromatographic Procedure. 35 g of air-dried starch carefully mixed with 0.35 g of calcium oxide calcined at 700-800°. To this mixture water was added, so that on taking the moisture content of the starch into consideration, the final water content of the mixture was 60% with respect to the absolutely dry starch. To this mixture was added 28 ml of chemically pure benzene and the mixture again carefully mixed. A chromatographic column was filled with this mixture in stages. The density of the column was regulated so that using the given amount of starch and a tube with a diameter of 17-18 mm the height of the column was 18 cm. Directly on top of this layer was placed a second layer, consisting of 2 g of starch, 0.9 g of calcium oxide which had not been calcined, and 1 ml of water. The height of the top layer was 1.5-2.0 cm.

1 ml of the test aqueous solution of the amine salts was introduced into the chromatographic column. A pressure of 180 mm was set up in the system. The mobile phase used was either butanol, or, in the case of multicomponent systems, a mixture of butanol and benzene in the proportion of 30: 70. The eluate was collected in a flask containing 15-20 ml of water containing 2-3 drops of bromothymol blue and was continuously titrated with 0.05 N hydrochloric acid.

The first to issue from the column was combined n- and i-propylamines which have the lowest partition coefficient; these were followed by ethylamine, and last methylamine. The end of the elution of one amine and the beginning of the elution of the next amine was evident from the temporary cessation in expenditure of acid for titration when a continuous supply of the mixture of butanol and benzene was passed through the column. When the titration results are presented graphically, they appear in the form of series of steps on a curve relating amount of acid used and amount of benzene supplied. The amount of the individual amines (and, consequently, of the original nitroparaffins) was calculated by means of the formula

$$\frac{a\cdot 100}{2\cdot b},$$

where a is the amount of 0.05 N acid used in titrating the eluate issuing from the column from the beginning until the appearance of the first step (for determination of the amount of nitropropanes); from the first step to the second (for calculating the amount of nitroethane), and from the second step to the end (for the determination of the amount of nitromethane); b is the amount of 0.1 N alkali used for titrating total amines during determination of total basicity.

Results for the analysis of mixtures of the nitroparaffins are given in Table 2.

The chromatographic method described does not permit the possibility of a separate determination of the 1- and 2-nitropropanes, since the partition coefficients of the corresponding amines in the systems water-organic solvents are very close. Nevertheless, 2-nitropropane is readily determined photometrically [9]. Combination of the chromatographic method with the photometric method makes it possible to determine all the components of a four-component system fairly rapidly and without the use of complicated apparatus.

Table 3 contains the results for an analysis of two four-component mixtures, obtained by the chromatographic and photometric methods.

TABLE 3

Analysis of Mixtures of Nitroparaffins

Sample no.	Analytical method	Found, %					
		1-and 2-nitropropanes	nitroethane	nitromethane	2-nitropropane	1-nitropropane	total
1	Chromatography	73,0	16,4	10,6	—	—	—
	Photometry	—	—	—	27,7		
	Combination of chromatography and photometry		16,4	10,6	27,7	45,3	100,0
2	Chromatography	59,6	23,6	16,7	—	—	—
	Photometry	—	—	—	27,6		
	Combination of chromatography and photometry		23,8	16,7	27,6	32,0	100,1

SUMMARY

It has been shown that it is possible to use partition chromatography for the analysis of mixtures of primary alkylamines with carbon chains of varying lengths.

The accuracy of the analysis is determined by the accuracy of the chromatographic separation of the alkylamines and amounts to ± 5-7% relative, on the average.

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DETERMINATION OF CARBONYL COMPOUNDS BY MEANS OF THE REACTION WITH AMINES

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The reaction between aldehydes and amines, leading to the formation, as a rule, of anils or Schiff bases $RCHO + H_2NR_1 \rightarrow RCH:NR_1 + H_2O$ was suggested by Schiff[1] for the quantitative determination of primary amines. The method consists of titrating the amine with a solution of enanthic aldehyde; the end point is taken as the cessation of the appearance of a turbidity from the water liberated at the point where the titrant drops into the solution. In the course of many years this reaction has not found application in the quantitative analysis of either amines or aldehydes. Only in 1944 was this method suggested for the determination of various amines, the water liberated during the reaction being determined by titration with Fischer reagent [2]. Two articles were published in 1953 in which the same reaction was used, but for the determination of aldehydes [3,4]. The amount of aldehyde is measured from the amount of amine used up, the latter being determined by titration, in the first article potentiometrically, in nonaqueous solvent by means of a solution of salicylaldehyde [3], in the second article by a solution dioxanesulfurtrioxide (the complex of sulfur trioxide and dioxane). Laurylamine [3] and aniline [4] were used as the amines. The authors of both articles came to the same conclusion, namely, that their methods are only applicable for the determination of aromatic aldehydes.

Apparently, the anils of aliphatic aldehydes are less stable than those of aromatic aldehydes and are destroyed during titration with acids. During the potentiometric titration of aliphatic aldehydes it has not been possible to get a jump on the curve.

We made it our aim to find conditions which will also ensure determination of aliphatic aldehydes by the reaction with amines. Doubtless, the formation of anils accurs quantitatively in the case of aliphatic aldehydes also, this being shown by complete liberation of water during a Schiff titration [1], and by the results of work [5] on the determination of citral, citronellal, and cinnamic aldehyde by the reaction with aniline, the amount of aldehyde being estimated in this case on the basis of the amount of water liberated during the reaction, the water being distilled from the reaction mixture and measured in a Dean and Stark apparatus.

It seemed to us that for the determination of aliphatic aldehydes it would be more expedient to measure the amount of water liberated during the reaction, and not the amount of amine used up. Determination of water could be carried out most accurately, of course, by titration with Fischer reagent [7].

Some authors are mistakenly of the opinion that is impossible to determine water by the Fischer method in the presence of carbonyl compounds [6], and are convinced that it is necessary to convert tha latter beforehand into the cyanhydrins. Nevertheless, the author of the Fischer method has indicated that it is possible to titrate water directly in carbonyl compounds.

Table 1 contains some of our results on the direct determination of the water content of various aldehydes. The accuracy of the determination was established by titrating known amounts of water added beforehand to the aldehyde.

The reaction between Fischer reagent and aldehydes is so slow that it does not interfere with water determination. The choice of an amine for reacting with the aldehydes is determined by two considerations: the amine

TABLE 1

Aldehyde	Weight taken, g	Fischer reagent used, ml[*]	Water content of the aldehydes	Added water found, g
Lauric	0,2710	3,02	2,0	
»	0,2710			
+ water	0,015	11,88	2,0	0,0159
Methylnonylacetaldehyde	0,5140	1,3	0,05	
»	0,5140			
+ water	0,0144	9,30	0,05	0,0144
Citral	1,010	2,94	0,53	
»	1,010			
+ water	0,0174	12,66	0,53	0,01745
Methoxybenzoic	1,1571	3,3	0,51	
»	1,1571			
+water	0,0202	14,51	0.51	0,02018
Piperonal	1,065	0,59	0,5	
»	1,065			
+water	0,0160	9,49	8,5	0,01602

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[*] In terms of a millimolar solution; 1 ml = 1,8 mg water.

TABLE 2

Aldehyde	Weight taken,g	Fischer reagent used ml	Found, %	
			by reaction with amine	by oxime formation
Benzaldehyde	0,4813	44,5	98,2	98,6
»	0,3200	30,15	99,9	100,2
Vanillin	0,3083	20,5	101,2	100,5
»	0,2300	15,0	99,3	
Piperonal	0,2076	13,8	99,7	100,2
»	0,3463	23,3	100,7	
Methoxybenzaldehyde	0,3495	25,3	98,6	99,5
Salicylaldehyde	0,4925	39,85	96,9	98,5
Nitrobenzaldehyde	0,1063	6,98	99,5	
»	0,2253	14,97	100,5	100,0
Dimethylaminobenzaldehyde	0,2639	17,7	100,0	100,0
»	0,2770	18,6	100,1	
Enanthic aldehyde	0,3062	24,2	90,1	91,3
Methylnonyl acetaldehyde	0,0924	4,95	98.7	99,5
n-Isopropylmethylhydrocinnamic aldehyde	0,1294	6,48	94,9	96,6

should react fairly rapidly with the aldehydes, and should have a high dissociation constant so as not to interfere with the direct titration of the reaction mixture — in which the amine is in excess — with Fischer reagent. The most suitable amines were found to be aniline and o-toluidine, depending on the conditions.

Our studies showed that aromatic aldehydes react quantitatively with o-toluidine, immediately after addition of a benzene solution of the amine, while the water which is liberated during the reaction can be titrated with Fischer reagent directly in the reaction mixture. There is no need to wait for 30 minutes or one hour, as suggested previously.

Table 2 contains results obtained during the direct titration of the water liberated during the interaction of aldehydes with o-toluidine. Some aldehydes-enanthic aldehyde, citral, α-methyl, n-isopropyl, hydrocinnamic, and methylnonylacetaldehyde — also react quantitatively, but considerably more slowly during the gradual titration of water. Such a determination is not convenient, since, as test showed, the free amine also reacts with Fischer reagent. Accordingly, we should like to suggest another method for the determination of aliphatic aldehydes.

The amount of water liberated during the reaction is determined after its removal from the reaction mixture by distillation with benzene. Complete removal of such small amounts of water (30–40 mg) by distillation presented great difficulty.

TABLE 3

Weight of water, g	Benzene distilled over, %	Water found, % in the distillate	Water found, % in the residue
0,0422	50	50,1	49,7
0,0480	60	68,0	31,8
0,0372	86,5	75,0	24,9
0,0310	100,0	97,0	2,75
0,0406	100,0	99,7*	
0,0425	100,0	99,8*	

* In the presence of aniline.

A study of the conditions necessary for the quantitative distillation of water was carried out on aliquots of water alone. It would appear on the basis of the azeotropic ratios for mixtures of benzene and water (91,17 : 8,83 % wt.) that such small amounts of water should come over completely with the first drops of benzene; however, as experiment showed, water is quantitatively distilled over, only when all the benzene used as the solvent has been distilled over. Presumably this phenomenon can be explained by the formation of a solution of water in benzene. An apparatus with ground glass joints was used for distilling the water.

Table 3 contains the results obtained during a study of the conditions necessary for complete distillation of water. These conditions were observed during the determination of aliphatic aldehydes. Both o-toluidine and aniline can be used as the amine in this case.

By distilling the water it was established that the reaction with amines proceeds quantitatively for all the aldehydes studied (Table 4) — both aliphatic and aromatic — and that this technique can be used as a method for the determination of these aldehydes.

Aromatic ketones of the acetophenone type do not react with amines, and, accordingly, do not interfere with the determination of the aldehydes (Table 5). The method is being studied further.

Determination of the Water Content of Aldehydes. An aliquot of the aldehyde (liquid aldehydes -directly; solids-in solution in methanol) was titrated with Fischer reagent until the first distinct appearance of the color of iodine.

In order to check on the accuracy of the determination, a known amount of water (0.015-0.020 g) was added to an aliquot of the aldehyde whose % H_2O had already been established, and this water again titrated with Fischer reagent.

TABLE 4

Aldehyde	Weight, g	Fischer reagent used, ml	Aldehyde found, % by reaction with amines	Aldehyde found, % by oxime formation
Acetaldehyde	0,089	19,0	94,0	94,5
Formaldehyde	0,0933	11,0	35,4	35,0
Propionaldehyde	0,0833	9,65	67,0	67,0
Enanthic aldehyde	0,3148	26,7	96,8	96,2
»	0,3225	27,35	96,7	
Methylnonylacetaldehyde	0,4780	26,0	100	
»	0,1185	6,36	98,5	99.5
Citral	0,1910	12,55	99,8	
»	0,2682	17,69	100,3	99 0
Citronellal	0,3570	22,4	97,0	
»	0,2825	17,75	96,8	96,5
Hydroxycitronellal	0,2570	15,2	102,0	
»	0,1784	10,55	102,1	99,0
Cinnamic aldehyde	0,3898	28,95	98,0	
»	0,4122	30,1	96,5	96,0
α-Methyl-n-isopropylcinnamic aldehyde	0,1736	8,79	96,3	96,6
»	0,2542	12,9	96,5	
α-Amyl-n-isopropylcinnammic aldehyde	0,3503	15,9	91 8	
»	0,1631	7,44	92,2	92,0
Benzaldehyde	0,2319	21,3	97,3	96,8
Vanillin	0,1549	10,18	99,9	100,3
Methoxybenzaldehyde	0,1487	10,9	99,6	100,5
Piperonal	0,1540	10,21	99,5	99,9
Salicylaldehyde	0.2450	19,94	99,2	99,5
Protocatechuic aldehyde	0.1279	9,27	100,0	
Nitrobenzaldehyde	0,2852	18,9	100,0	99,8

Determination of Aldehyde by Direct Titration. To 0.2-0.4 g of aldehyde was added 5-10 ml of a 15% solution of o-toluidine or aniline in benzene, after mixing, the mixture was immediately titrated with Fischer reagent to a distinct brown color. A blank was carried out at the same time. The water content of the aldehyde was determined on a separate aliquot:

$$\%\ \text{aldehyde} = \left(\frac{(a-b)\cdot T\cdot 100}{W} - c\right)\cdot\frac{M}{18},$$

where a is the amount of Fischer reagent used up for the test solution, in ml; b is the amount of Fischer reagent used up for the blank, in ml; T is the titer of the Fischer reagent expressed in g of water; W is the weight of aldehyde, taken; c is the moisture content of the aldehyde, in %; M is the molecular weight of the aldehyde.

In all cases the purity of the aldehyde was checked by formation of the corresponding oxime [8].

A Study of the Conditions for Distilling Off the Water. The apparatus used for distilling the water consisted of a pear-shaped flask ~ 100 ml, connected by means of bent tube to a condenser, which was connected in turn through an adapter provided with a calcium chloride guard tube, to the receiver — a 50-100 ml conical flask; all connections were made of ground glass.

An aliquot of water (30-40 mg) was placed in the flask and 15 ml of benzene added; in the last two experiments (Table 3) 1.25 g of aniline was added in each case. In order to keep the temperature constant the flask was heated on a vaseline bath. When a temperature of 150° had been reached heating was stopped and the flask kept at this temperature for some time; the flask was then removed from the bath but was not disconnected from the apparatus; after cooling to room temperature, the flask was disconnected and the condenser washed, by passing 15 ml of anhydrous methanol through the connecting tube which was turned round; the distillate collected in the receiver, and the residue in the distillation flask were titrated separately with Fischer reagent. Washing with methanol was essential since a considerable part of the water was held in the condenser.

TABLE 5

Carbonyl compounds	Aldehyde content of the mixture, %	
	taken	found
Acetophenone		
Benzaldehyde + acetophenone	65,4	67,0
Methylacetophenone		
Benzaldehyde + methylacetophenone	65,3	65,9
Ditto	29,1	28,7
» »	9,9	10,6
Methoxyacetophenone		
Benzaldehyde + methoxyacetophenone	64,5	65,7
Ditto	25,4	25,0

A General Method for the Determination of Aldehydes (Aromatic and Aliphatic). To 0.15-0.4 g of the aldehyde was added 15 ml of a solution of aniline in benzene; the flask, connected beforehand to the apparatus, was placed in a vaseline bath and heated to 40-60°; the water was then distilled off as described above and the condenser washed down with methanol.

A blank experiment was run in parallel in which no aldehyde was used, while the moisture content of the aldehyde was determined separately.

Determination of Certain Ketones and Their Mixtures with Aldehydes. Determination was carried out on the basis of the reaction with a benzene solution of o-toluidine, the water being titrated directly in the reaction mixture.

SUMMARY

It has been shown that both aromatic and aliphatic aldehydes react quantitatively with amines to liberate one molecule of water. Measurement of the amount of water liberated during this reaction can serve as a method for the quantitative determination of the aldehyde. It has been shown that it is possible to carry out a direct determination of the water content of aldehydes by means of Fischer reagent.

Two methods are suggested for the determination of aromatic and aliphatic aldehydes on the basis of their reaction with amines, followed by titration of the water with Fischer reagent.

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BRIEF COMMUNICATIONS

THE SPECTROPHOTOMETRIC DETERMINATION OF MAGNESIUM IN URANIUM

N. N. Krot, A. P. Smirnov-Averin and A. G. Kozlov

The necessity very often arises in analytical practice of determining small amounts of magnesium in uranium and its compounds. The present article is devoted to a discussion of the use of a very sensitive reagent for magnesium — eriochrome black T— for this purpose.

Eriochrome black T (or chromogen black special ET-00) gives colored complexes with many cations. Several authors have used eriochrome black T for the determination of magnesium in various materials [1-5]. Nevertheless no method has been published for the determination of magnesium in solutions of uranyl salts.

Working Solutions and Apparatus. A 0.1% solution of eriochrome black T was prepared by dissolving an aliquot of the purified, recrystallized [6] dye in twice-distilled methanol. Such a solution is stable for more than two months.

An ammoniacal buffer solution with a pH of 10.2 was prepared by dissolving 54 g of twice recrystallized ammonium chloride in 500 ml of 25% aqueous ammonia, and making the volume up to one liter. Working solutions of uranium were prepared from spectrographically pure uranyl nitrate; the solutions were standardized gravimetrically. All experiments were carried out in quartz vessels using specially purified water. Spectrophotometric measurements were made on a Beckman type "DU" spectrophotometer. A type LP-5 tube potentiometer was used for measuring the pH by means of a glass electrode.

The Stability of Aqueous Solutions of Eriochrome Black T and of its Complex with Magnesium. A study of the stability of aqueous solutions of eriochrome black T and of its complex with magnesium is essential in order to assess the permissible length of time between preparation of the solutions and measurement of their optical density. Such experiments were carried out by adding 3 ml of the ammoniacal buffer solution and 1 ml of the 0.1 % solution of eriochrome black T to 30-40 ml of a solution with a known magnesium sulfate content. The optical density of the solutions was measured in the course of 4 hours at various wavelengths.

These experiments showed that the optical density of solutions of eriochrome black T in a pure form, or with additions of various amounts of magnesium, decrease linearly with time to the extent of 0.3-0.8% in 30 minutes. No increase in density was observed in any of the tests; it may be assumed therefore that the equilibrium of complex-formation is established rapidly.

Determination of the Composition of the Complex*. In order to choose the optimum wavelength region, light absorption curves were taken for a solution of pure eriochrome black T, and of a solution of the dye containing magnesium in sufficient excess to suppress dissociation of the complex. As is evident from Fig. 1, the greatest difference in the optical densities of the solutions of eriochrome black T and of solutions of its complex with magnesium is observed at 500-550 mμ and 640-690 mμ. However, only the spectral region at 500-550 mμ is suitable for accurate measurements, since at wavelengths of 640-690 mμ the results show poor reproducibility.

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* D is the optical density of the solution; M is the molar concentration of a solution of the compound whose formula is given below to the right of the designation; E is the molar extinction coefficient of the solution of the same compound; n is the number of molecules of eriochrome black T which interacts with one ion of magnesium.

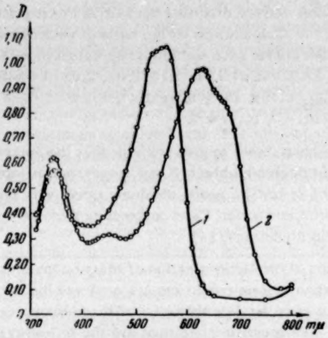


Fig. 1. Light-absorption curves for a solution of pure eriochrome black T (Curve 2) and a solution of the latter containing excess magnesium (curve 1).

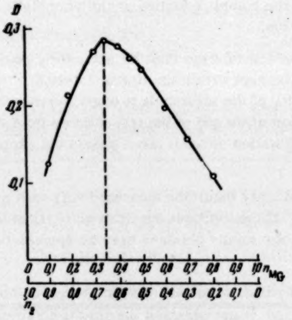


Fig. 2. Deviation of the optical density from additivity composition of the solution. D) Deviation of the optical density of a solution of eriochrome black T and magnesium from additivity; n_E) the molar fraction of eriochrome black T in solution; n_{Mg}) the molar fraction of magnesium in solution.

The composition of the complex formed between magnesium and eriochrome black T at a pH of 10 was studied by the Ostromyslenskii-Job method [7,8] and by calculation.

By means of a rigorous mathematical analysis N. P. Komar' [9] has shown that the Ostromyslenskii-Job method is not applicable to all cases. In our case this method is applicable in the form in which it is used for the study of the composition of compounds formed from colored reagents.

As is evident from Fig. 2, maximum deviation of the optical density from additivity is observed at molar ratios of eriochrome black T to magnesium of 2: 1, i. e. the complex formed has a composition expressed by the formula $(MgE_2)^{4+}$ (where E represents the anion of the dye).

Similar curves were also obtained at 500, 510, 530, and 540 mμ. In the course of this work it was established that the position of the maximum is independent of the wavelength at which the optical density is measured. Obviously, one can conclude from this that only one complex occurs in solution at pH 10; this is confirmed by published data [1,8].

In Fig. 3 are given the curves relating optical density of the solution to magnesium concentration for a constant concentration of the dye of 4.67×10^{-5} mole/liter. The composition of the complex can be calculated from this curve also.

Actually, the optical density D of a solution with an initial concentration M_E of eriochrome black T and a concentration M_{MgE_n} of the complex, at a wavelength for which the molar extinction coefficients of the dye and the complex are E_E and E_{MgEn} respectively, will be determined by the equation

$$D = (M_E - nM_{MgE_n}) E_E l + M_{MgE_n} \cdot E_{MgE_n} l, \quad (1)$$

where n is the stoichiometric coefficient of the reaction for the formation of the complex.

The values of E_E and E_{MgEn} can be determined by measuring the optical density of a solution of the dye to which no magnesium has been added (D_0), and of a solution of dye containing excess magnesium (D_0'), sufficient to suppress dissociation of the complex

$$E_E = D_0 / M_E l, \quad (2)$$

$$E_{MgE_n} = D'_0 n / M_E \cdot l. \quad (3)$$

Simultaneous solution of equations (1), (2), and (3) gives the expression:

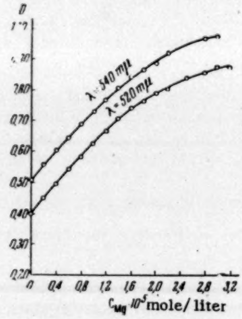
$$n = \frac{(D - D_0) M_E}{(D'_0 - D) M_{MgE_n}}. \quad (4)$$

If the initial concentration of magnesium M_{Mg} is small in comparison with the concentration of the dye, then almost all the magnesium will be combined as the complex, i. e. $M_{Mg} \cong M_{MgE_n}$, and expression (4) can be written in the form

$$n = \frac{(D - D_0) M_E}{(D'_0 - D_0) M_{Mg}}. \quad (5)$$

Cation impurities (in excess, 100 x Mg concentration)	Magnesium taken, γ	Magnesium found, γ	Relative error, %
—	4,73	4,87	3,0
—	9,45	9,29	1,7
—	9,45	9,48	0,3
—	4,73	4,67	1,3
Fe^{3+}	7,48	4,65	1,7
Co^{2+}	9,45	9,44	0,1
Ni^{2+}	9,45	9,71	2,7
Cr^{3+}	4,73	4,67	1,3
Al^{3+}	9,45	9,68	2,4
MoO_4^{2-}	4,73	4,82	1,9

Fig. 3. Relation between optical density of the solution and magnesium concentration for a constant concentration of eriochrome black T. D) The optical density of the solution; C_{Mg}) magnesium concentration, mole/liter.



The expression derived describes the initial linear parts of the curves Fig. 3. Calculations on the basis of points located on these parts of the curves gave the following values of n: 1.86 1.88; 1.92; 1.92 (λ = 520 mμ) 2.10; 2.10; 2.02, 2.02 (λ = 540mμ) respectively for C_{Mg} 0.15 x 10^{-5}; 0.2 x 10^{-5}; 0.3 x 10^{-5} and 0.4 x 10^{-5} mole/liter, i. e., n ≈ 2.

Thus, it has been shown by two methods that the composition of the complex of eriochrome black T and magnesium is represented by a ratio of 2: 1. The result obtained agrees with those of Harvey, Komarmy, and Wyatt[1] and contradicts those of Schwarzenbach and Biedermann [6].

The Accuracy of the Determination of Magnesium in its Pure Solutions. When certain conditions are observed the maximum experimental error for determination of magnesium does not exceed ± 3%. The requisite conditions are the following:

1. The magnesium concentration of the test material should lie within the limits 0.1-0.4 γ/ml. The necessity for conforming to such a comparatively narrow range of magnesium concentrations is explained on the one hand by the intense color of eriochrome black T, and on the other hand, by the comparatively low stability of the complex formed at the very high sensitivity of the reaction.

2. The pH of the test solution must be accurately controlled. The pH must be kept within the limits 9.8-10.6. Since the optical density of the solution is strongly dependent on the acidity, deviation of the pH of the test solution from the value at which the calibration curve is taken should not exceed the limits of ± 0.1.

3. The optical density should be measured very soon after preparing the solution. If the solutions are allowed to stand for more than 30 minutes, the results obtained may be appreciably low.

4. Only twice-distilled water and purified reagents should be used. If this condition is not observed the results obtained will be appreciably high.

Procedure for the Determination of Magnesium in the Presence of Uranium. Uranium, even in small amounts interferes with the determination of magnesium, since it interacts with eriochrome black T to form a colored product. Interference from uranium can be suppressed by masking it with ammonium carbonate or hydrogen peroxide. The presence of carbonate ions in solution, however, leads to low results for magnesium. Hydrogen peroxide on the other hand rapidly destroys eriochrome black T.

Accurate determination of magnesium in uranium is possible after removal of uranium from solution by precipitation with 8-hydroxyquinoline at a pH of about 5 [10]. All the magnesium remains in the filtrate under these conditions. Excess 8-hydroxyquinoline and traces of uranium can be removed by extraction with chloroform. Such ions as Fe^{3+}, Cr^{3+}, Co^{2+}, Al^{3+}, MoO_4^{2-}, and Ni^{2+}, which occur in uranium as impurities, are coprecipitated with the uranium and do not interfere with magnesium determination.

As a result of experimental work, the following method has been developed for the determination of magnesium in the presence of uranium.

Test solution containing not less than 5 γ of magnesium is placed in a quartz beaker. After neutralization of excess acid, the volume of the solution is made up to 20-25 ml, and to it is added 5 ml of acetate buffer (10 ml of concentrated HCl added to 380 ml of a 50% solution of CH_3COONa and the volume made up to 1 liter). The solution is heated to 70-90° and a 10 % solution of 8-hydroxyquinoline in acetone added to it in sufficient amount to precipitate the uranium and the impurities present in the latter. The precipitate is coagulated by boiling the; solution for 3-5 minutes the precipitate is then filtered off and washed with hot water. The filtrate and wash liquors are collected in a separating funnel. Excess 8-hydroxyquinoline and traces of metals remaining in solution are extracted by means of five small to portions(10-15 ml)of chloroform. The aqueous phase is filtered in order to remove drops of chloroform. The solution obtained, or an aliquot of it, after adjusting the pH the requisite value with ammonia, is placed in a 50 ml standard flask. To this flask is added 1 ml of a 0.1% solution of eriochrome black T in methanol and the volume made up to the mark; the solution is carefully mixed. The optical density of the solution is measured at 250 mμ with respect to distilled water as reference solution.

The calibration curve is constructed by taking 10-15 samples of a standard $MgSO_4$ solution covering the magnesium concentration range from 1γ to 30 γ, and diluting them to 25-30 ml; the pH is then adjusted and the solutions transferred to 50 ml standard flasks; 1 ml of the dye solution is added to each of the flasks and the volumes made up to the mark. After mixing, the optical density of the solutions is measured and the results plotted on a graph of "optical density" against " magnesium concentration".

The table contains the results for several determinations of magnesium in pure uranium and in uranium containing impurities.

The method permits determination of 0.005% (and higher) of magnesium in uranium with a relative error of not more than ± 3%. Determination can be carried out in hydrochloric, nitric, sulfuric, or acetic acid media. Small amounts of phosphate ions do not interfere (not more than 20 times the amount of magnesium present).

When the optical density is measured on a FÉK-M colorimeter with a green filter the experimental error does not exceed ± 5%.

SUMMARY

A method is described for the spectrophotometric determination of small amounts of magnesium in uranium by means of eriochrome black T. The composition of the colored compound of magnesium with eriochrome black T has been studied.

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TITRIMETRIC DETERMINATION OF MOBILE ALUMINUM IN SOILS

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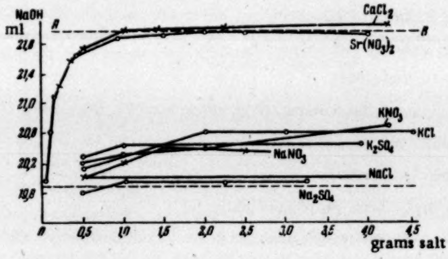
The most often used for determining aluminum and acid in salt extracts of soil is that of Sokolov [1]. This method consists in titrating free acid plus aluminum with alkali, in one aliquot of the solution, the aliquot being heated to the boil, and titration being carried through to the phenolphthalein endpoint; in another aliquot of the same extract the aluminum is complexed with sodium fluoride and the free acid titrated. Aluminum is determined by difference.

The method has a number of disadvantages, namely: during the first titration aluminum hydroxide is precipitated, but formation of basic salts is also possible; the precipitate can adsorb alkali; the presence of a precipitate complicates observation of the titration endpoint. As a result, the method gives high results for aluminum and results with poor reproducibility.

In view of these disadvantages of Sokolov's method we have adopted a titrimetric method of determining aluminum suggested by Pavlinova [2]. The method is based on the capacity of aluminum salts to react with alkali metal tartrates with the liberation of an equivalent amount of acid which is titrated to the phenophthalein endpoint. When this technique is used the solution remains clear right up to the endpoint. The endpoint is more distinct in the presence of foreign salts. In the absence of foreign salts the solution acquires a rose color up to the equivalence point and the results are low.

The effect of the salts of the alkali and alkaline-earth metals is shown in the diagram.



The dotted line AB in the diagram shows the theoretical amount of alkali. The curves obtained in the presence of $CaCl_2$ and Sr $(NO_3)_2$ almost agree with the theoretical straight line for solutions containing from 2% to 7% of $CaCl_2$ or not less than 5% $Cr(NO_3)_2$.

The reaction proceeds according to the following equation

$$4\,AlCl_3 + 3\,K_2C_4H_4O_6 + 4\,H_2O = K_6Al_4(C_4H_2O_6)_3\,O_2\,(OH)_2 + 12\,HCl.$$

The intercomplex compound which aluminum forms with tartrate, presumably, partially hydrolyzes with formation of KOH; $CaCl_2$ is therefore added to suppress the hydrolysis.

When the test solution contains free acid the latter is titrated with the aluminum. The free acid is determined by adding 10 ml of a 10% solution of potassium oxalate, neutralized beforehand to phenol red, to the extract, and the acid titrated with alkali using the same indicator. The difference in the amount of alkali used for the first and second titrations corresponds to the amount of mobile aluminum, since aluminum, on reacting with tartrates liberates 3 g. equivalents of acid, then 1 ml of 0.1 N alkali corresponds to 0.009 g aluminum.

Preliminary experimental work led to the development of the following method for determining aluminum. To 80 g of soil is added 200 ml of 1 N KCl solution and the whole agitated on a shaker; the mixture is then filtered. The free acid is determined in one aliquot of the filtrate by the method described above, while the total acidity is determined in another. The total acidity is determined by adding 5 ml of a 20% solution of potassium sodium tartrate, neutralized to phenolphthalein, to 25-100 ml of the soil extract, and the mixture titrated with 0.5 N alkali to a distinct red color; 40% $CaCl_2$ solution is then added in such an amount that the final concentration of $CaCl_2$ in the total volume is about 3%; this solution is titrated slowly, dropwise, until a rose color is reached, making sure that the turbidity which develops after the addition of each drop dissolves before adding the next drop. The percentage content of aluminum is calculated by means of the formula

$$Al = \frac{(V - V_2) \cdot N \cdot 0{,}009 \cdot 200 \cdot 100}{80\, V_2},$$

where V is the volume of alkali used for neutralizing the total acidity; V_1 is the volume of alkali used for titrating the free acidity; V_2 is the volume of extract taken for titration; and N is the normality of the alkali.

In order to check the proposed method, aluminum was determined in the same extracts by the suggested tartrate method, and by either a gravimetric method, or a hydroxyquinoline method with a titrimetric finish, and all the results compared with those obtained by Sokolov's method. During the gravimetric determinations aluminum hydroxide was precipitated with ammonium sulfate in the presence of ammonium chloride, since, according to Lyass'er's results [3], the temperature at which aluminum hydroxide is dehydrated depends on the method of precipitation, and in the given instance is equal to 414°, while during precipitation with ammonia the temperature is 1100°.

Small amount of iron and manganese were determined photometrically. Since these metals also liberated acid from tartrates, the volume of alkali used up in neutralizing the acid liberated by these metals was calculated, bearing in mind that iron liberated three equivalents and manganese one equivalent of acid. The results obtained are given in the table.

No. of extract	NaOH 0.004347 N used, ml	Amt. of alkali equiv. to Fe + Mn, ml	Al found, %					
			by free acid, ml	by tartrate method, ml	gravimetrically	hydroxyquinoline method	Sokolov's method
1	8,80; 8,75	0,055	0,075	0,0340	0,0338	—	0,0360
2	12,60; 12,55	0,145	0,175	0,0479	0,0479	—	—
3	2,90; 2,90	0,052	0,100	0,0107	0,0101	0,0103	0,0135
4	2,13; 2,10	—	0,202	0,0075	—	0,0076	—
5	2,23; 2,15	—	0,220	0,0038	—	0,0039	—
6	8,02	—	0,280	0,0151	—	0,0146	—
7	1,220	—	0,418	0,0008	—	0,0008	—
8	1,412; 1,388	—	0,260	0,0022	—	0,0019	0,0029

Notes. In Expts, Nos. 1-4, 25 ml of soil extract was taken, while in Nos. 5, 6, and 8, 50 ml was taken, and in No. 7, 100 ml; in all experiments 5 ml of 20% tartrate, 10 ml of oxalate, and from 3 to 10 ml of 40% $CaCl_2$ were added. The free acid and aluminum in experiments No. 7 and 8 were titrated from a microburet.

SUMMARY

A new titrimetric method is suggested for the determination of mobile aluminum in soils. It has been shown that the proposed method is more accurate and more convenient than the generally used method of A. V. Sokolov.

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DETERMINATION OF MICROAMOUNTS OF ARSENIC BY MEANS OF A SOLUTION OF A DIVALENT CHROMIUM SALT.

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A solution of a divalent chromium salt was used for the first time for a reducing quinquevalent arsenic ions to the elemental (metallic) state by Shat'ko in 1938 during the development of a method for determining 0.26-45% of As in various minerals [1]. In subsequent work a solution of divalent chromium salt was used for determination of 0.1-0.01% of As in ores, casts, and steels, in zinc white, bunker dust, and zinc containing agglomerates [2], in salvarsan preparations and in urine [3] , in tin [4], and in other materials of industrial and sanitary-hygienic importance. The methods developed required large samples (5-10 g), since the sensitivity amounted to 0.39 mg in 100-200 ml of test solution [5].

Our object was to develop a technique for the accurate determination of less than 0.4 mg of arsenic. Small amounts of arsenic are usually isolated by means of ferric hydroxide[6,7] or manganese dioxide [8] used as collectors. In our method the collector used was copper metal produced during reduction with divalent chromium. Divalent copper is quantitatively reduced by Cr^{2+} ion to the elemental (metallic) state in neutral media [1]. Quinquevalent arsenic ions are reduced by Cr^{2+} ions to elemental arsenic in a strongly acid solution (30-40% by volume of HCl sp. gr. 1.19). Under these conditions copper ions remain in solution. Experiments showed that copper is not completely reduced in acid solutions; however, it is reduced in sufficient amount to trap the arsenic precipitate which has been reduced to the elemental state. Copper is then removed from the arsenic by means of ferric ammonium alum. Determination of elemental arsenic can be finished off gravimetrically, photometrically or titrimetrically.

When the gravimetric finish of Zhivanovich was used [9], filtration washing of the precipitated elemental metallic arsenic, and its separation from copper was carried out in a No. 4 Schott crucible. The arsenic remaining was washed with a solution of ammonium chloride and then with water saturated with carbon dioxide, and dried at 105° to constant weight. During determination of 2.2 mg of arsenic by this method, the following results were obtained 2.8, 2.4, 2.2, 2.0, 2.6, and 1.6 mg. The original solution of sodium hydrogen arsenate was standardized gravimetrically by Levol's method [10] and by means of Cr^{2+}[5]. Thus, satisfactory results can be obtained for the determination of down to 2 mg of arsenic in 100 ml. For lower arsenic contents we could not get satisfactory results.

For photometric determination, the arsenic in an elemental state (after separation from copper) was dissolved in sulfuric acid in the presence of hydrogen peroxide. Glucose was used as a reducing agent. During determination of 0.094 mg of As photometrically, the following values were obtained 0.160, 0.112, and 0.096 mg As.

Photometric methods [7,8,11] based on formation of molybdenum blue during the reduction of heteropolyacids are applicable to pure solutions obtained after removal of arsenic from other elements: phosphorus, silicon, boron, germanium, tin, zirconium, cerium, thorium, and other elements also form heteropolyacids, which, on reduction give a blue color.

For the titrimetric method of determining arsenic reduced by divalent chromium to the elemental state, 0.01 N I_2 and 0.01 N $Na_2S_2O_3$ were used as standard solutions. Titrations were carried out with the aid of a microburet. The results obtained are given in the table.

Determination of Arsenic (Elemental) by a Titrimetric Method

As, mg		As, mg	
taken	found	taken	found
0,094	0,114	0,26	0,26
0,094	0,100	0,26	0,28
0,094	0,110	0,26	0,27
0,094	0,110	0,02	0,03
0,094	0,113	0,04	0,03
0,094	0,114	0,02	0,02
0,094	0,110	0,02	0,01
0,26	0,27	0,04	0,04
0,26	0,27	0,02	0,02

For determination of microamounts of arsenic (of the order of 0.02 mg) in solution, the following technique can be recommended :

The test solution is evaporated on a water bath to a volume of 10-20 ml, and 3-5 ml of HCl (sp. gr. 1.19) and 2 ml of $CuSO_4$ (about 0.01 g Cu) added. CO_2 is bubbled through the solution and 7-10 ml of $CrCl_2$ (about 0.5 N $CrCl_2$) or $CrSO_4$ added, the whole is then heated to the boil in a current of CO_2 and boiled for 2-3 minutes. The precipitate is washed 2-3 times with a 2% solution of NH_4Cl, and the copper brought into solution by oxidizing with a solution of ferric ammonium alum (10 ml of a 40% solution). The metallic arsenic remaining on the filter is washed 2-3 times with HCl (1: 4) and then 2% NH_4Cl to a pH of 3.7 (methyl orange indicator); the arsenic is finally determined iodometrically as described in [4,5].

The method developed was checked on standard samples of bronze and brass. 0.5-2 g of bronze or brass was dissolved in nitric acid (sp.gr. 1.4) and 10-20 ml of sulfuric acid (1: 1) added to convert nitrates into sulfates (evaporation to the appearance of white fumes). After cooling, the dry residue was dissolved in distilled water and quantitatively transferred to a 150 ml flask. The solution was neutralized with sodium carbonate until no more CO_2 was liberated; twice its volume of about 0.5 N $CrCl_2$ solution was then added and the whole boiled for 3 minutes; the mixture was filtered through a fine filter (white band paper can be used) and the precipitate washed 2-3 times with 2% NH_4Cl, 10-20 ml of a 40% solution of ferric ammonium alum was finally added. The arsenic after its separation from copper, was washed 2-3 times with HCl (1:1) and then with 2% NH_4Cl to a pH of 3.75. The filter and precipitate were transferred to a flask, and 5 ml of 0.01 N I_2 and 3 ml of 2% $NaHCO_3$ added (the flask was covered with a watch glass), the solution was finally titrated after 15 minutes with $Na_2S_2O_3$.

For brass containing 0.002% As the following values were obtained: 0.002, 0.0016, 0.0015, and 0.0015 % As.

Antimony, lead, and the other components of bronze and brass do not interfere with the arsenic determination. No cupric sulfate is added for the determination of arsenic in bronze and brass.

The method gives accurate results, demands less time than other methods, and can be used for solving both industrial and sanitary-hygienic problems.

SUMMARY

A method has been developed for isolating microamounts of arsenic by means of a divalent chromium solution, using freshly precipitated (reduced by Cr^{2+} ions) metallic copper as a collector. Copper is removed from the arsenic by means of a solution of ferric ammonium alum. The arsenic which is left (in the elemental state) is then determined iodometrically. The sensitivity of the method is 0.02 mg of As in 100-200 ml. The method has been checked on standard samples of bronze and brass.

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A SIMPLIFIED SPECTROPHOTOMETRIC METHOD OF DETERMINING ORGANIC COMPOUNDS BY MEANS OF THEIR ABSORPTION IN THE NEAR INFRARED

Ts. N. Roginskaya and A. I. Finkel'shtein

Absorption spectra in the near infrared have found application in recent years for solving analytical problems, and for solving problems connected with the determination of the structure of materials [1,2]. In addition to precision spectrophotometric methods in the near infrared, simplified absorptiometric methods involving the use of light filters [3] for isolating the necessary spectral region, have also been used. The possibility is demonstrated in the present article of carrying out an absorptiometric analysis of certain mixtures of organic components which differ comparatively little from each other in their molecular structure.

The apparatus which is schematically shown in Fig. 1 was assembled for carrying out the analysis. In contrast to the usual schemes, we introduced the constant resistances R_1 and R_2, which facilitate measurement for low optical densities. FÉSS-U10 [4] silver sulfide photoelements were used for receiving the radiation. The measurement technique was the same as that used during the work with two-arm photocolorimeters. The cells used for working with organic liquids were made from glass tubes 30 mm in diameter and 200 mm long. These tubes had a side tube in the middle with a ground glass stopper. To the ground faces of the cells, windows were fastened by means of copper tightening washers fitted onto the cell by means of a cement made of glycerol and litharge. This same cement was used for smearing the faces of the cell before fitting on the windows. Cells made in this way proved to be sufficiently stable and suitable for work with the mixtures described below. The light filter used was the copper complex of monoethanolamine [3]. The concentration of the colored complex was chosen empirically so that at the maximum transmission of the light filter, it gave the highest concentration sensitivity. The following light filter answered these requirements most closely: 3.5 mg $CuSO_4 \cdot 5H_2O$ was dissolved in 50 ml of water and 10 ml of monoethanolamine added. The absorption spectrum obtained on the UM-2 monochromator with a germanium photoelement is shown in Fig. 2. The cells for the light filter were made from organic glass. The thickness of the absorbing layer was 10 mm. Calibration curves were used in each case for the determinations

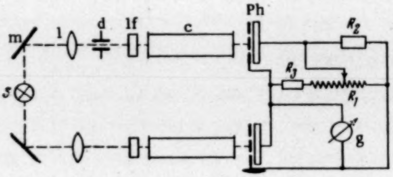

Fig. 1. Schematic diagram of the apparatus: S) Light source (incandescent lamp 6b, 21 c.p.); m) mirror; *l*) lens (F=10 cm); d) diaphragm; *l*f) light-filter (monoethanolamine complex of copper); c) cell; ph) photoelement; (FÉSS-U10); R_1 =75 ohms; R_2=50 ohms; R_3 = 750 ohms; G) galvanometer type GMP. GMP.

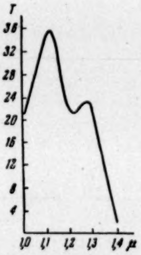

Fig. 2. Absorption spectrum of the light-filter (ordinate T,% abscissa λ, μ).

TABLE 1

Chlorex, %		Error, % %	
taken	found	absolute	relative
50,0	49,0	−1,0	2,0
40,0	37,5	−2,5	6,25
25,0	23,5	−1,5	6,0
15,0	14,5	−0,5	3,3
10,0	10,05	+0,5	5,5
5,0	4,8	−0,2	4,0

TABLE 2

Water, %		Error, % %	
taken	found	absolute	relative
4,05	4,10	0,05	1,23
5,70	5,80	0,10	1,75
7,47	7,50	0,03	0,40
12,01	12,0	0,01	0,83

(Fig. 3). In a previous article [5] we described a spectrophotometric method of analyzing a mixture of chlorex (β,β' dichlorodiethyl ether) and dichloroethane on the basis of their absorption spectra in the ultraviolet and infrared. In the same article we gave the absorption spectra of chlorex and dichloroethane in the near infrared, and indicated the possibility of developing a method which uses this region of the spectrum. Experimental work completely confirmed these suggestions. Table 1 contains the results for the analysis of synthetic mixtures. The mean relative error of 15 determinations of chlorex within the concentration range 5 to 40%, was about 7%. Such an error is quite acceptable for production control. Under the same conditions, similar results were obtained for the determination of water in isopropanol (Table 2). The sensitivity threshold of the method in this case proved to be about 1%. The highest accuracy was found in the limits 1-10% when a cell 200 mm long was used. The mean relative error of 10 determinations was about 2.5%, which corresponds to the accuracy of the usual photocolorimetric methods of analysis. Cyclohexanol in cyclohexanone (Table 3) was also determined. In this case the threshold sensitivity was about 5%, the mean arithmetic error was about 4%. An analysis took about 5-10 minutes in all three cases.

TABLE 3

Cyclohexanol %		Error, %	
taken	found	absolute	relative
4,95	5,5	+0,55	11,1
10,0	9,9	−0,10	1,0
19,9	22,0	+2,1	10,5
34,3	35,0	+0,7	2,04
49,7	51	+1,3	2,8

The results obtained show that even in the case where compounds with similar absorption spectra are analyzed, simplified methods of analysis in the near infrared can give satisfactory results.

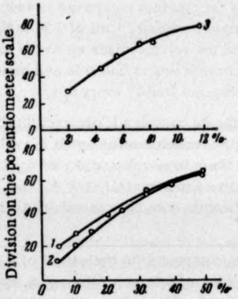

Fig. 3. Calibration curves for various determinations: 1) Chlorex in dichloroethane; 2) cyclohexanol in cyclohexanone; 3) water in isopropanol.

SUMMARY

It has been demonstrated that it is possible to analyze mixtures of organic compounds with similar absorption spectra in the $1-2\ \mu$ region by means of a simplified spectrophotometric method.

Taking as examples the determination of chlorex in dichloroethane water in isopropanol, and cyclohexanol in cyclohexanone, the potentialities of simplified absorptiometric methods for control production of organic chemicals has been demonstrated.

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DETECTION AND DETERMINATION OF RHENIUM

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Pottassium perrhenate in the presence of hydrochloric acid, divalent tin, and sulfite, gives a colored compound. The conditions for carrying out the reaction have been studied on a FÉK-M photocolorimeter using supplementary light-filters whose characteristics are similar to those of Ilford light filters [1].

As preliminary experiments showed, color developments depends on acid concentration. From Table 1 it is clear that the best results are obtained for a concentration of about 4 g-equivalents/liter of hydrochloric acid (taking into account the acid contained in the stannous chloride solution). Further increases in acidity lead to rapid development of turbidity in the solution as a result of the deposition of the compound $Sn_5O_5Cl_{10}$, which is insoluble in hydrochloric acid [2]. In the presence of sulfuric acid hydrolysis takes place more intensely. Oxalic, tartaric, and citric acids are used for slowing hydrolysis of tin compounds. The best results were obtained in our case with citrate ions at a concentration of 0.04 mole/liter. The optimum concentration of stannous chloride was found to be 0.22 mole/liter, while that for sodium sulfide was 0.04 mole/liter. 15-20 minutes was found to be sufficient for complete color development. The rate with which the color develops, and its intensity, increase on addition of alcohol. Nevertheless, in the presence of 5 ml of ethanol a turbidity develops in 10-13 minutes.

The color intensity depends on the order in which the reagents are added. The optimum color is observed when the following order is adopted: to a 25 ml flask containing the solution of the rhenium compound is added 10 ml of hydrochloric acid (2:1) and 2 ml. of 0.5 M sodium citrate, and the mixture cooled, 1 ml of 1 M sodium sulfite is then added, followed by 1 ml of a 5% solution of stannous chloride, and the volume made up to the mark with distilled water. The optical density is measured after 20 minutes. Solutions of stannous chloride and sodium sulfite change in air accordingly; they be protected from the air or should be prepared freshly every day.

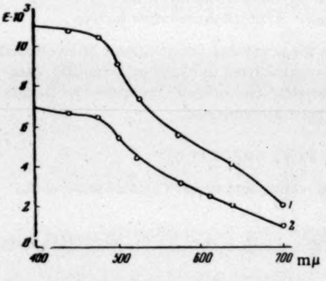

Fig. 1. Absorption curves of the rhenium complex: 1) In aqueous solution; 2) in the isoamyl alcohol layer.

Maximum absorption by the Re complex is observed in the ultraviolet (Fig. 1). The molar extinction coefficient is 1.1×10^4. Solutions conform to Beer's law down to concentrations of 8 γ of rhenium/ml (Fig. 2). The relative experimental error for the photometric determination of rhenium does not exceed 7% (Table 2).

The presence of vanadium compounds to the extent of 0.2 mg. and of nitrate ions to the extent of 0.1 mole/liter does not interfere with rhenium determination. Ions with an intrinsic color (nickel, chromium, and cobalt) increase the color intensity. Molybdates and tungstates also interfere.

A study of the possibility of extracting the rhenium complex with benzene, toluene, chloroform, isoamyl acetate, diethyl ether, butanol, and isoamyl alcohols. The colored rhenium compound was found to be extracted with butanol and isoamyl alcohol. The color is stable for one hour in the alcohol layer. The absorption curve of the extract is shown in Fig. 1.

TABLE 1

Effect of Acidity on the Color of the Solution (Re-93γ ; 1 ml of 1M Na_2SO_3 2 ml of 0.5 M sodium citrate; 1 ml of $SnCl_2$; volume -25 ml; time 20 min.)

Acid concentration, g. equivalent/liter	Relative density
1,4	0,03
2,0	0,15
2,8	0,85
4,0	0,97
4,6	Becomes turbid after 14 min
5,4	Becomes turbid after 6 min

TABLE 2

Photometric Determination of Rhenium with Sulfite

Rhenium, γ		Error, γ
taken	found	
2,8	2,8	0,0
5,6	5,8	+0,2
8,4	7,9	−0,5
13,0	13,9	−0,9
18,6	18,2	−0,4
27,9	27,0	−0,9
55,8	54,7	−1,1
74,4	74,4	0,0
111,6	109,6	−2,0

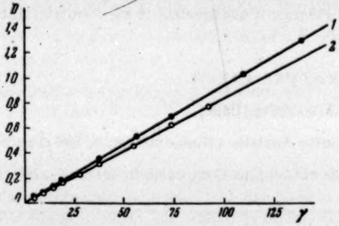

Fig. 2. Conformity to Beer's law: 1) aqueous solution, volume 25 ml; 2) isoamyl alcohol layer volume 11 ml; a light filter with transmission at 400 mμ was used.

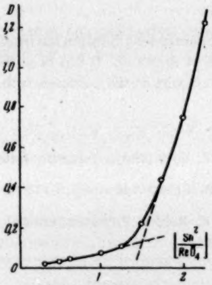

Fig. 3. Optical density of the solutions for variable stannous chloride concentrations.

The molar extinction coefficient is less in the alcohol layer than in the aqueous layer, and amounts to 6.9×10^3. Thus, extraction with isoamyl alcohol permits the sensitivity of the method to be increased only by transferring the sulfite complex into the alcohol layer which is smaller in volume. The extract in isoamyl alcohol conforms to Beer's law (Fig. 2).

In order to detect rhenium, its solution contained in a 100 ml separatory funnel is prepared as described above. After 20 minutes, 11 ml of isoamyl alcohol is added. The whole is shaken for 30 seconds, and the layers allowed to separate; the lower aqueous layer is rejected. The colored alcoholic layer is often turbid because of the formation of a stable emulsion. Accordingly, it is poured through a dry filter paper 3 cm in diameter into a 30 mm cell. Photometric measurements are made with a light-filter whose transmission is located at 400 mμ. Isoamyl alcohol is used as the reference solution.

Rhenium can be detected by adding 2 ml of concentrated hydrochloric acid to a test tube containing 2 ml of a test solution which contains perrhenate; the whole is thoroughly mixed and 0.25 ml of 1 M sodium sulfite and 0.25 ml of a 5μ solution of stannous chloride dissolved in concentrated hydrochloric acid added. The color develops with time and is compared with distilled water after 3-5 minutes. After standing for 10-15 minutes, the solution becomes turbid. This method permits detection of as little as 0.5γ rhenium. Those elements which interfere during the quantitative determination also interfere here.

The sign of the charge of the ion of the rhenium complex formed was determined by ion exchange chromatography. For this purpose the colored solution was passed through a column containing the cation exchange resin SBS in the H-form. The filtrate obtained was colored. On passing the test solution through a column filled with the anion exchange resin TN in the OH-, Cl-, and SO_4-forms, the ion exchange resins became colored while the filtrate obtained was colorless. When the anion exchange columns were subsequently elute with hydrochloric and sulfuric acids, the resin was decolorized and the eluate was colored. Thus, the behavior of the complex on ion exchange resins indicates that its colored part is the anion.

The valence of rhenium was determined photometrically [3]. Stannous chloride solution was prepared by dissolving tin metal in concentrated hydrochloric acid in a hydrogen atmosphere. Potassium perrhenate, chemically pure grade, was dissolved in distilled water on heating. In order to get the colored solution, the amounts of rhenium and stannous chloride taken were calculated, and the concentrations of the acid, sulfite, and citrate were the same for the determination of rhenium. The break on the curve in Fig. 3 is located at a point corresponding to a ratio of $[Sn^{2+}]:[ReO_4^-] = 1.5$. The oxidation – reduction process which occurs during formation of the complex compound, can be expressed by the scheme

$$2ReO_4^- + 3\,Sn^{2+} + 12H^+ = 2ReO^{2+} + 3\,Sn^{4+} + 6H_2O$$

Consequently, rhenium is quadrivalent in this complex.

SUMMARY

A new reaction for rhenium has been developed. Conditions have been developed for the quantitative and qualitative determination of rhenium. It has been shown that rhenium is quadrivalent in the rhenium sulfite complex, and that the colored part of the complex is the anion.

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A NEW PHOTOMETRIC METHOD FOR THE DETERMINATION OF NICKEL

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The ammonium salt of purpuric acid – murexide – $C_8H_8N_6O_6H_2O$, which is used for determination of water hardness and for the photometric determination of calcium [1], reacts with nickel salts in a weakly ammoniacal medium and changes its color from purple-red to orange yellow. By means of aqueous murexide it is possible to detect as little as 0.2 γ of nickel in 1 ml of solution at a limiting dilution of $1:5 \times 10^6$.

The reaction is carried out by adding 0.2 ml of 0.5% ammonia solution and 0.05 ml of a 0.02% aqueous solution of murexide to 1 ml of test solution.

Salts of the alkali and alkaline-earth elements, Mo^{VI}, V^V, W^{VI}, Pd^{II}, $Pt^{II,IV}$, Zr^{IV}, Th^{IV}, Nb^V, Ta^V, Au^{III}, Te^{IV}, Se^{IV}, Be, Ag, Cd, AsO_4^{III}, PO_4^{III} and Cu^{II} do not interfere with detection of nickel.

Fe^{II}, Fe^{III}, Co^{II}, Pb^{II}, and Mn^{II} salts do not react with the reagent but large concentrations interfere with the reaction.

Only zinc and magnesium salts react with murexide in a weakly ammoniacal medium, changing its color from purple-red to orange-yellow. The sensitivity of the reaction with zinc is 1γ in 1 ml at a limiting dilution of 1: 1,000,000 while for magnesium the sensitivity is 20γ in 1 ml at a limiting dilution of 1: 50,000. Presumably, zinc and magnesium react with murexide in the same way as nickel, as a result of the similarity in the radii of their ions. A 0.02γ aqueous solution of murexide can be used for the photometric titration of nickel. The color obtained on adding an aqueous solution of murexide to a weakly ammoniacal solution containing nickel in the concentration range 0.2 γ to 5γ in 1 ml of solution, conforms to Beer's law. Excess reagent interferes by virtue of its own color, accordingly, the method of colorimetric titration is used. We have established that 0.2 ml of a 0.02γ aqueous solution of murexide corresponds to 1 γ of nickel.

The colorimetric titration method of determining nickel in steels consists of the following. 0.10-0.20 g of steel is dissolved on boiling in sulfuric acid (1: 9), 1 ml of hydrogen peroxide is then added in order to oxidize Fe^{II} to Fe^{III}; the acid solution is neutralized by ammonia, the latter being added until the iron is almost precipitated (pH 6.2-6.4). To the weakly acid solution is added 10 ml of 0.5 N zinc sulfate and the whole mixed. 10 ml of 1 N $K_3[Fe(CN)_6]$ is then added and the precipitate of $Zn_3[Fe(CN)_6]_2$ containing all the nickel filtered off [2-3], the precipitate is washed several times with water. To the precipitate on the filter is added excess 5% NaOH in which the $Zn_3[Fe(CN)_6]_2$ dissolved, while traces of iron and nickel in the form of their hydroxides remain on the filter. The sodium hydroxide should be free from carbonate. Iron and nickel hydroxides are dissolved in sulfuric acid (1: 9) and excess acid neutralized with ammonia, the latter being added in excess; the mixture is then boiled. The solution containg the ammoniacal complex of nickel is boiled to remove excess ammonia and collected in a 100 ml standard flask (or in a larger flask in the case of a high nickel content). All these operations are necessary for concentrating traces of nickel and for separating it from the major part of the iron. The volume of the solution of the ammoniacal complex of nickel is made up to the mark with water, the solution is thoroughly mixed and a 10 ml aliquot of the solution used for the photometric titration with murexide. The aliquot is titrated with a 0.02% aqueous solution of murexide to the appearance of an orange-yellow color, and the color compared with a series of standard, titrated solutions of nickel. The series of standard, titrated solutions of nickel are prepared as follows. Into 10 titration tubes with flat bottoms and fitted with ground glass stoppers, are introduced 10 ml lots of nickel standard solutions containing 0.5, 1, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, and 5.0 γ of nickel in 1 ml of solution. To each tube is added 1 ml of a 0.5 % ammonia solution and the whole mixed. After mixing, 1,2,3, 4,5,6,7,8,9, and 10 ml of a 0.2 % aqueous solution of murexide is added to the series of tubes, and the contents of the tubes mixed. Aqueous solutions of murexide are not particularly stable, the intensity of the purple color decreases in the course of 3-5 days; accordingly, the reagent and the series of standard titrated solutions should be prepared on the day they are to be used.

Results for the determination of nickel in steels are given in Table 1.

The method gives good results: the insignificant deviations obtained are quite permissible for a photometric method.

Subsequently, in order to check the method and to establish the effect of low concentrations of cobalt, the following determinations were carried out. 0.10 g of steel whose nickel content had been determined beforehand, was dissolved in sulfuric acid (1: 9); known amounts of nickel and cobalt salts in the form of solutions were then added; the mixture was treated with hydrogen peroxide in order to oxidize Fe^{II} to Fe^{III}, and the procedure outlined above for the determination of nickel in steel subsequently followed.

TABLE 1

Determination of the Nickel Content of Steel by means of Murexide (0.1 g of steel was taken, the solution was diluted to 100 ml)

Ni content, %	Ni found %	Difference
0,10	0,10	0,00
0,12	0,11	0,01
0,14	0,13	0,01
0,15	0,15	0,00
0,18	0,17	0,01
4,20	4,00	0,20

It is clear from Table 2 that for ratios of Ni: Co = 1: 10 the method gives good results.

TABLE 2

Determination of Nickel in the Presence of Cobalt in Steels using Murexide

Ni content, %	Ni added, %	Co added, %	Ratio Ni : Co	Total Ni content, %	Ni found, %	Difference
0,10	0,05	0,5	1: 3	0,15	0,14	0,01
0 12	0,08	1,0	1: 5	0,20	0,19	0,01
0,14	0,06	1,0	1: 5	0,20	0,20	0,00
0,15	0,10	2,5	1 : 10	0,25	0,23	0,02
0,18	0,32	5,0	1 : 10	0,50	0,50	0,00

SUMMARY

A 0.02% aqueous solution of murexide -ammonium purpurate— $C_8H_8N_6O_6 \cdot H_2O$ reacts with the nickel ammonia complex, and its color changes from purple-red to orange - yellow. The limit of identification is 0.2 γ of nickel in 1 ml of solution at a limiting dilution of 1: 5,000,000.

The color of the solutions conforms to Beer's law. A new colorimetric titration method has been developed for the determination of nickel in steels.

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AMPEROMETRIC DETERMINATION OF COBALT BY AN IODOMETRIC METHOD USING A ROTATING PLATINUM MICROELECTRODE

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Results for the determination of cobalt in ammoniacal media by direct titration with ferricyanide are somewhat low because of the partial oxidation of cobalt by dissolved atmospheric oxygen.

An iodometric method for the determination of cobalt in an ammoniacal medium, which was suggested recently, enables correct results to be obtained even in the presence of dissolved atmospheric oxygen [1].

Taking this fact into account, and also bearing in mind the ease with which free iodine is reduced on a platinum electrode, we decided to investigate the possibility of carrying out an iodometric titration of cobalt in an ammoniacal medium, using an amperometric technique for establishing the endpoint. The setup plus the rotating platinum microelectrode have been described before [2].

The concentration of the original solution of chemically pure cobalt sulfate was established by the sulfate method. The working solutions of iodine and sodium arsenite were prepared by taking accurately weighed aliquots of freshly distilled iodine, and chemically pure arsenic oxide.

During a direct amperometric titration of an ammoniacal solution of cobalt with the iodine solution it was established that, in the absence of excess iodine, the reaction between cobalt and iodine proceeds too slowly as a result of which the titration process takes too long. Thus, from a practical point of view, direct titration of cobalt with iodine in the presence of ammonia and ammonium citrate, on the basis of the formation of iodopentamminocobaltinitrite, proved unsuitable. Positive results were obtained, however, during determination of cobalt by titration of excess iodine with sodium arsenite.

Cobalt was determined as follows: a known volume of a standard solution of cobalt was introduced into a 100 ml beaker used as the titration flask, and 25 g of ammonium nitrate added; the solution obtained was then brought up to room temperature. To this solution was then added from a buret a standard iodine solution in such amount that not less than 1-2 ml of standard sodium arsenite would be required for titrating the excess iodine. 5 ml of 18% ammonia solution was next added, followed by sufficient water to bring the final volume of the solution to 40-50 ml . After standing for 5-10 minutes the excess iodine was titrated with the standard sodium arsenite added from a 5 ml microburet, at a cathodic polarization of the microelectrode of 0.1 volt.

During the initial stages of the titration, the sodium arsenite was added in large portions without measuring the current. The current was only measured at a high galvanometer sensitivity when most of the iodine had been reduced. From this point onward the reagent was added dropwise. Adoption of such a technique ensured that a clearly defined titration curve with a steep left branch was obtained. Titration did not take more than 2-3 minutes

As Table 1 shows, the titration results are sufficiently accurate and show good reproducibility. The smallest concentration of cobalt was approximately 0.01 mg/ml.

Dissolved oxygen has no effect on the accuracy of the determination.

Sulfate, nitrate , acetate, tartrate, and chromate do not interfere with titration of cobalt even when the molar concentration of these anions exceeds that of cobalt 100 times 'Table 2).

TABLE 1

Determination of Various Amounts of Cobalt (average of 4-5 parallel determinations)

Cobalt taken, mg	Cobalt found, mg	Mean dev. of one determ. from mean		Dev. of mean value found from taken	
		in mg	in %	in mg	in %
51,38	51,84	0,02	0,04	0,46	0,89
25,44	25,45	0,11	0,43	0,01	0,04
20,50	20,50	0,04	0,19	0,00	0,00
15,36	15,38	0,05	0,31	0,02	0,13
10,28	10,19	0,01	0,14	0,09	0,87
5,13	5,14	0,03	0,43	0,01	0,19
2,54	2,54	0,01	0,47	0,00	0,00
1,54	1,55	0,01	0,80	0,01	0,64
1,03	1,04	0,01	0,72	0,01	0,97
0,51	0,48	0,02	4,16	0,03	6,00

TABLE 2

Effect of Foreign Ions on the Results of Titrating 20 and 50 mg of Cobalt (average of 3 cobalt determinations)

Foreign salt	Mol. ratio of foreign ion to cobalt	Cobalt found, mg	Max. dev. from mean, %	Dev. of means found from taken	
				in mg	in %
Effect of anions					
Ammonium sulfate	100	20,53	0,10	0,02	0,10
Ammonium citrate	100	20,54	0,14	0,04	0,19
Ammonium tartrate	100	20,44	0,34	0,06	0,29
Ammonium acetate	100	20,61	0,19	0,11	0,53
Ammonium nitrate	1000	20,49	0,39	0,01	0,05
Ammonium chloride	1	19,91	0,42	0,59	2,87
Ditto	0,01	20.44	0,14	0,06	0,29
Potassium chromate	50	20,55	0,53	0,05	0,24
Effect of cations					
Calcium nitrate	50	20,62	0,24	0,12	0,58
Strontium nitrate	50	20,60	0,43	0,10	0,48
Barium nitrate	50	20,69	0,14	0,19	0,92
Magnesium sulfate	10	20,67	0,10	0,17	0,82
Ditto	1	20,46	0,05	0,04	0,19
Zinc nitrate	100	20,48	0,14	0,02	0,10
Aluminum nitrate	20	20,30	0,20	0,20	0,97
Ditto	40	20,04	0,20	0,46	2,23
Ferric sulfate (III)	10	20,77	0,24	0,27	1,31
Ditto	5	20,65	0,19	0,15	0,73
Nickel nitrate	10	20,98	0,38	0,48	2,34
Ditto	5	20,60	0,14	0,10	0,48
Cadmium acetate	20	20,73	0,19	0,23	1,12
Ditto	10	20,64	0,10	0.14	0,67
Copper nitrate	15	20,70	0,24	0,20	0,97
Ditto	10	20,61	0,19	0,11	0,53
Lead nitrate	40	20,26	0,29	0,24	1,17
Ditto	20	20,42	0,19	0,08	0,39
Bismuth nitrate	10	20,80	0,05	0,30	1,46
Ditto	5	20,46	0,24	0,04	0,14
Chromium nitrate	1	19,88	0,10	0,62	3,02

Chloride ions interfere; they depress the results; chlorides are only tolerated in small amounts (of the order of 1% of the cobalt). Presumably, chloride ions enter into the inner sphere of the complex instead of iodide ions.

Calcium, strontium, barium, zinc, magnesium, aluminum, trivalent iron, nickel, cadmium, copper, lead, bismuth, even in large amounts do not interfere. During titration, aluminum, iron, and bismuth ions were kept in solution by addition of ammonium citrate, while excess potassium iodide was added to keep lead in solution. Cr^{3+} ions interfere; they were accordingly oxidized to chromate. Divalent manganese, even in small amounts, interferes. Manganese was therefore oxidized by potassium permanganate in an acid medium in the presence of fluoride ions, using the amperometric technique for establishing the endpoint. To the cobalt solution to be titrated and containing various amounts of manganese, was added 4 ml of 2 M sulfuric acid, and 20-25 g of ammonium fluoride, after which the manganese was oxidized with permanganate, the latter being added dropwise, until the current arising from the oxidation of Mn^{2+} ion on the microelectrode was kept at +0.6 volt. After the manganese had been oxidized, the cobalt was determined in the solution thus obtained by the method described above. In this way it was found possible to get sufficiently accurate results, as long as the manganese concentration did not exceed that of the cobalt.

SUMMARY

It has been shown that it is possible to titrate cobalt amperometrically by an iodometric method using a rotating platinum microelectrode. The method gives reasonably accurate results for the determination of cobalt alone, and for its determination in the presence of many foreign ions. One of the advantages of the method is that dissolved atmospheric oxygen does not interfere.

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DETERMINATION OF NaOH, Na_2CO_3, and $NaHCO_3$ IN THEIR MIXTURES BY AN ELECTROMETRIC NONCOMPENSATING METHOD*

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In a previous paper [1] we published examples of the application of an electrometric noncompensating method of titrating acid mixtures containing nitric, sulfuric, phosphoric, and chromic acids such mixtures being difficult to deal with from an analytical point of view. The present article is devoted to the use of an electrometric noncompensating method for titrating another mixtures which is interesting from the analytical point of view, namely a mixture of NaOH, Na_2CO_3, and $NaHCO_3$.

Titration of solutions of these alkalis is carried out by means of a tungsten electrode paired up with a copper sulfate electrode which serves as the reference electrode. Its construction has been described in a previous article [2].

The indicator electrode (Fig. 1) is made from a tungsten wire or spiral connected by means of tin to a copper wire. The tungsten wire 1 whose thickness is not less than 0.2 mm is fitted into a small sleeve filled with molten tin 3. The sleeve is soldered to a copper wire 4. The tungsten wire should be at least 3.5 cm long. The copper wire is about 15 cm long while its thickness is 2-3 mm. After the tin has cooled down the electrode is firmly fastened to the copper wire. The point at which the tungsten wire is fixed, and all the sleeve, is covered with any type of lacquer or with BF-2 universal glue.

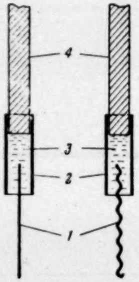

Fig. 1. Contructional details of the tungsten electrode.

The procedure for electrometric noncompensating titration and the arrangement of the electrodes in the solution being titrated have been described previously [1].

Quinhydrone, antimony, molybdenum, and tantalum electrodes were tested in the course of the work described here as indicator electrodes for titrating the solutions of the alkali mixtures, in addition to the tungsten electrode. The best electrodes proved to be the tungsten and molybdenum electrodes. Such widely used electrodes as the antimony and quinhydrone electrodes were found to be less sensitive to changes in H^+ ion concentration than the tungsten electrode.

The relatively high sensistivity of the tungsten electrode to hydrogen ions has been noted before; Kolthoff and Furman [3] referring to the work of Bayliss, point out that the potential of the tungsten electrode changes by 90 millivolts for a change of one in the pH, i. e., it is 90-58 = 32 millivolts greater than the potential of the hydrogen electrode.

The molybdenum and tantalum electrodes are similar in properties to the tungsten electrode, but these electrodes are less sensitive to hydrogen ions than tungsten.

In our work the alkali mixtures were invariably titrated with 0.1 N HCl. The volume of the solution being titrated was always 50 ml. Titration was carried out with an external resistance of R = 5000 ohms.

Determination of NaOH. The titration curve for NaOH is shown in Fig. 2.

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[*] L. E. Sud'bina carried out the experimental work.

During titration of a strong acid by a strong base (and vice versa) by means of a compensating method, the equivalence point on the titration curve corresponds to the break on the curve (point m), at which dE/ dv has a maximum value. In contrast to the compensating method, however, in the electrometric noncompensating method of titrating the equivalence point does not lie at point m, but is somewhat lower. The equivalence point on the curves obtained during noncompensating titration is determined by the intersection of the two tangents as shown in Fig. 2 (point c). The amount of acid used for titrating the NaOH is determined by the projection of point c into the abscissa (point v).

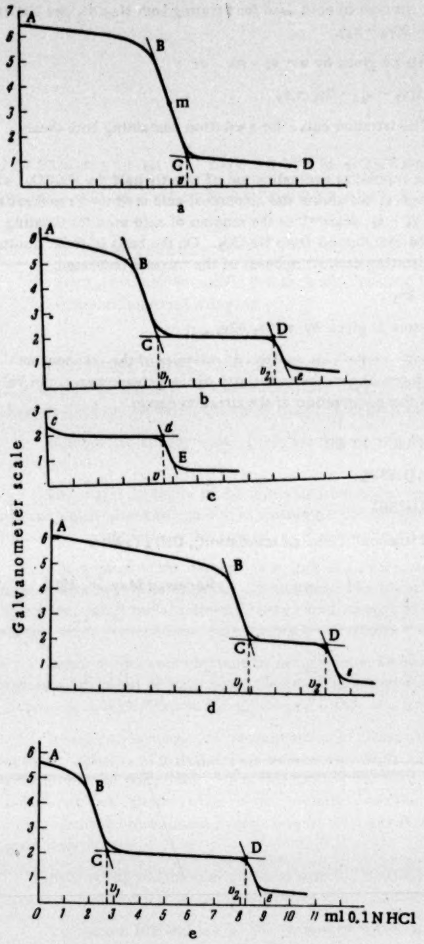

Fig. 2. Titration curves for: a) NaOH; b) Na_2CO_3; c) $NaHCO_3$; d) NaOH + Na_2CO_3; e) Na_2CO_3 + $NaHCO_3$.

Determination of Na_2CO_3. The titration curve for a solution of Na_2CO_3 is shown in Fig. 2.

The steplike form of the titration curve is explained by the fact that neutralization of sodium carbonate by hydrochloric acid proceeds in two stages:

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$

$$NaHCO_3 + HCl \rightarrow H_2CO_3 + NaCl.$$

Neutralization of sodium carbonate according to the first equation proceeds along the part abc, while neutralization of the bicarbonate thereby formed proceeds according to cd. At point d decomposition of sodium bicarbonate is complete, after which the potential of the indicator tungsten electrode changes as a result of addition of excess HCl.

The amount of acid used for neutralizing the Na_2CO_3 is determined by point c, or on the abscissa by v_1. The total amount of acid used for neutralizing all the Na_2CO_3 is determined by d, or , on the abscissa by v_2. From this, it follows that the acid used for neutralizing the $NaHCO_3$ will be given by $\Delta v = v_2 - v_1$.

Determination of $NaHCO_3$. The titration curve is shown in Fig. 2c.

Here as in the previous curve (Fig. 2b) the interaction between HCl and $NaHCO_3$ proceeds according to cd on the titration curve. The equivalence point corresponds to point d, or , on the abscissa to v.

Analysis of Mixtures of NaOH and Na_2CO_3. The titration curve for a solution containing both these components is shown in Fig. 2d.

During a titration of this mixture, NaOH is initially neutralized,being the stronger base ; Na_2CO_3 is then neutralized, and finally the $NaHCO_3$ formed. abc corresponds to the process of neutralizing total NaOH and half the Na_2CO_3. Titration of the $NaHCO_3$ formed, i. e. the second half of Na_2CO_3, is shown on the curve by cd. Points c and v_1 determine the acid used for titrating total NaOH and half the Na_2CO_3, while points d and v_2 determine the total expenditure of acid for titrating both components of the alkali mixture. From this, it follows that the difference $\Delta v = v_2 - v_1$, equal to section cd, should determine the amount of acid used for titrating the $NaHCO_3$ formed.

Using these relationships, it is possible to find the amount of acid used for titrating both Na_2CO_3 and NaOH. The acid used for titrating Na_2CO_3 should be $v = 2\Delta v = 2(v_2 - v_1)$.

While for titrating the NaOH, the acid used for will be given by $v = v_1 - \Delta v$ or

$$v = v_2 - 2(v_2 - v_1) = 2v_1 - v_2 .$$

Analysis of a Mixture of Na_2CO_3 and $NaHCO_3$. The titration curve for a solution containing both these components is shown in Fig. 2e.

Here, as for titration of Na_2CO_3 alone, the part abc represents neutralization of exactly half the Na_2CO_3, while cd represents titration of sodium bicarbonate. Points c and v_1 determine the amount of acid used up for neutralizing half the Na_2CO_3 in solution. cd, or the difference $\Delta v = v_2 - v_1$, determines the amount of acid used for titrating all the $NaHCO_3$, i. e., the $NaHCO_3$ already in solution and that formed from Na_2CO_3. On the basis of these results it is possible to determine the amount of acid used for titrating each component of the mixture indicated.

The acid used for titrating Na_2CO_3 is given by $v = 2v_1$.

The acid used for titrating the $NaHCO_3$ in the mixture is given by $v = v_2 - 2v_1$.

The accuracy of the electrometric noncompensating method for analysis of mixtures of the components indicated lies within the limits ± 0.5 - 1.0% relative, depending on the sensitivity of the galvanometer, the value chosen for the external resistance R, and the accuracy of the construction of the titration curves.

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DETERMINATION OF THE GYPSUM CONTENT OF CEMENT BY MEANS OF CATION-EXCHANGE RESINS

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The methods currently used in cement factories for the determination of the gypsum content of cement [1,2] are not satisfactory. A method we have developed which is based on the use of cation exchange resins is characterized by the ease with which it can be carried out, by high accuracy, and speed (30-35 minutes).

Methods are already known [3-6] for the determination of the sulfate content of solutions by means of cation exchange resins.

The major difficulty in the determination of the gypsum content of cement is the choice of a suitable solvent which would be capable of getting all the cement sulfates into solution, touching as little as possible of the remaining components in the process, so that the extract does not contain too many cations.

The gypsum in the cement* was first of all extracted by means of distilled water: 0.5 g of cement was treated with 100 ml of water for 10 minutes. The water extract contained calcium in the form of sulfate and hydroxide, alkali metal sulfates, a very small amount of the aluminum in the form of aluminates, and soluble silicic acid. Nevertheless, only 0.5 % SO_3 was obtained from several examples of cement extracted in this way.

Better results were obtained on using a more agressive solvent 5% boric acid solution. On treating 0.5 g of cement with 25 ml of boric acid, 30-50% of the aliquot dissolved, while the SO_3 content of the insoluble residue dropped to 0.05-0.07% and did not exceed 0.15%; this was fully permissible.

In order to decrease the decomposition of clinker materials we chose a combined method of extracting the sulfates: aliquots of material were treated with 25 ml of water and the insoluble residue treated on the filter with a 5% solution of boric acid. When this method was used, 20-30% of the material in the form of sulfates, borates, and silicates of calcium, magnesium, and alkali metals, dissolved. On passing such a solution through a column of cation exchange resin in the hydrogen form the equivalent amount of sulfuric acid, and also of boric and silicic acids were formed.

By titrating the solution obtained with 0.1 N alkali solution using methyl orange as indicator, the gypsum content of cement was determined. Under these conditions boric and silicic acids were not titrated.

To extract 10% and less of the gypsum from the cement it was necessary to treat 0.5 g of sample with 25 ml of distilled water with continuous agitation for 10 minutes. The solution was filtered and the insoluble residue washed initially 2-3 times by decantation, and then washed 3-4 times on the filter with 5% boric acid. The filtrate and wash liquors were passed successively through the resin column at a rate of 3-4 ml per minute; the column was then washed with 50-70 ml water at the same rate, and the total solution, about 100 ml in all, titrated with standard alkali solution using methyl orange as indicator.

The column which was 1 cm in diameter was filled with cation-exchange resin to a height of 17-20 cm.

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* Some alkali metal sulfates are found in the clinker part of the cement; these sulfates, usually, as in the given case, are determined together with the sulfate part of the gypsum.

The cation exchange resin was kept overnight in distilled water and then transferred, using water, into the column in which a lump of glass wool had been placed beforehand; a few glass beads were placed on top of the glass wool. There should be no air bubbles among the cation exchange resin grains, otherwise, the exchange rate is depressed. The column prepared in this way was washed 3-4 times with 3 N hydrochloric acid in order to convert the resin into the H-form, the acid was passed through at the rate of 3-4 ml per minute. The column of resin in the H-form was then washed with distilled water until the wash liquors gave a neutral reaction with methyl orange; the test solution was finally passed through.

The method gives fully satisfactory results (table); the deviation does not exceed 0.15% absolute, when compared with the results of the gavimetric method.

5-6 determinations can be carried out without regenerating the resin. It is necessary check for complete absorption of the cations by adding ammonium oxalate to the solution obtained after titrating the last filtrate (after the sixth determination) with alkali. The absence of any precipitate indicates that the result obtained is correct. When a precipitate appears then the column should be regenerated immediately by passing 70-100 ml of 3-4 N hydrochloric acid through it, and washing with distilled water until the washing give no reaction for chloride ions.

Образец	SO_3 content, %				By the gravimetric method	SO_3 content of the insoluble residue, %
	Cation exchange method					
	1	2	3	mean		
Clinker from the Vorovskii factory + 10% $CaSO_4$	4,75	4,71	4,81	4,75	4,84	0,03
Zdolbunovskii cement	3,17	3,22	3,13	3,17	3,25	0,15
Volkhovskii factory cement	1,42	1,47	1.38	1,42	1,47	0,10
Vorovskii factory cement	1,30	1,33	1,27	1,30	1,31	Traces
Bukhtorm construction cement	1,56	1,61	1,52	1,56	1,56	0,13
Kolenerg construction cement	2,25	2,30	2,25	2,27	2,40	0,14
Putsolanov Portland cement	0,87	0.73	0,78	0,78	0,81	0,07
Pikakevskii cement	2,38	2,31	2,28	2,32	2,34	Traces

At the end of the working day the cation exchange resin should also be regenerated with hydrochloric acid, washed two-three times with water, and then, before starting a new determination on the following day, the column should be washed with water until the eluate gives a neutral reaction to methyl orange.

It is best to have 2-3 columns, one of which is being regenerated while the others are being used for the determinations.

It should be pointed out that sulfide sulfur present in cement is not determined when this technique is used. Accordingly, the true gypsum content of the cement is given by the cation exchange method.

The technique developed can be successfully used for controlling the amount of gypsum in many cement factories.

SUMMARY

A method which has been developed for the determination of the gypsum content of cement is based on treatment of the cement with a 5% solution of boric acid, which readily dissolves gypsum and hardly touches the cement base clinker; the solution which is obtained is passed through a column containing a cation-exchange resin in the H-form, and the eluate obtained titrated with sodium hydroxide using methyl orange as indicator.

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QUANTITATIVE DETERMINATION OF ACENAPHTHYLENE

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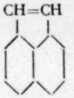
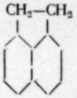
As a consequence of the increased interest in recent years in acenaphthylene (I) as available raw material for the production of plastics, the question of its quantitative determination in the product obtained by the dehydrogenation of acenaphthene (II) has acquired practical importance. Depending on the dehydrogenation conditions, there is a complex mixture of acenaphthylene, unchanged acenaphthene, and large or small amounts of colored and colorless by-products. Quantitative determination of acenaphthylene in such a complicated mixture on the basis of the sparingly soluble acenaphthylene picrate [1,2] is very difficult and is always accompanied by large losses. A photometric method described in the literature by Kynaston and Jones [3] and by Kaufman and Williams [4], for the determination of acenaphthylene was developed using a Spekker absortiometer in conjunction with a mercury lamp. The accuracy of this method is 1%.

I



II



For the quantitative determination of acenaphthylene we studied a number of method based both on its unsaturated character and on its intense yellow color. The investigations were carried out on synthetic mixtures of acenaphthylene and acenaphthene. After unsuccessful attempts to determine acenaphthylene by Margoshes' method, we made a careful study of the possibility of determining acenaphthylene by combining it with bromine according to a method described by Isagulyants and Egorova [5]. The method takes into account the halogen used up for the addition reaction as well as for substitution reactions. This is a very important point since the acenaphthylene and acenaphthene present in the test material are readily halogenated. Even this method, however, did not give satisfactory results. When the acenaphthylene content of the test material was high we got low results, while for low contents of acenaphthylene the results were far too high. This is explained by the fact that in addition to incomplete combination of bromine with the double bond of the five-membered ring, there occurs combination of the bromine with the naphthalene nucleus without liberation of hydrogen bromide.

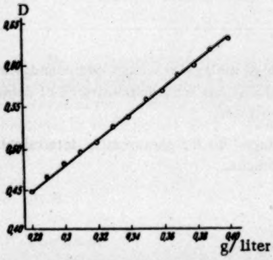
We tried to make use of the capacity of acenaphthylene to polymerize under the action of mineral acids to form a sparingly soluble polymer, hoping in this way to develop a gravimetric method of determining acenaphthylene. The polymerizing agent used was a solution of sulfuric acid in glacial acetic acid. In order to reduce losses during the determination, the latter was carried out in a centrifuge tube, so that it was possible to avoid filtering and transferring the precipitate. A description is given below of a gravimetric method which has been developed as the result of protracted research.

Into a dry tared centrifuge tube is weighed 0.3-0.4 g of test material, which is then dissolved by heating in 1 ml of glacial acetic acid. 1 ml of sulfuric acid (8 g of concentrated sulfuric acid in 20 ml of glacial acetic acid) solution is then added to the hot solution obtained and the whole heated for 15 minutes in a metal block at 125-130° while it is continuously stirred. The contents of the tube are diluted with 5 ml of water and the whole heated to the boil, the precipitate which is formed is ground up for some time with a rod and the contents of the tube finally centrifuged. The clear supernatant liquid is decanted and the polymer which remains is washed

TABLE 1

Gravimetric Determination of Acenaphthylene in Polymeric Form

Acenaphthylene content of the mixture, %	Weight mixture, g	Polymer obtained	Acenaphthylene found, %	Acenaphthylene content of the mixture, %	Weight mixture, g	Polymer obtained	Acenaphthylene found, %
100	0,4120	0,3886	94,32	80	0,4064	0,3463	85,21
100	0,4252	0,4038	94,97	80	0,4118	0,3424	83,15
100	0,4095	0,3884	94,85	70	0,4170	0,3141	75,32
100	0,4118	0,3383	94,29	70	0,4200	0,3176	75,62
90	0,4071	0,3641	89,44	60	0,4130	0,2895	70,10
90	0,4216	0,3831	90,87	60	0,4302	0,2983	69,34
90	0,4032	0,3599	89,26	50	0,4067	0,2298	56,50
90	0,4125	0,3652	88,53	50	0,4114	0,2434	59,16
80	0,4042	0,3410	84,36				



Relation between optical density (D) and acenaphthylene concentration (c).

with 4 ml of alcohol, the tube being heated in the block and the polymer ground up with a rod. After two alcohol washings, the tube plus polymer are placed in a drying oven and dried for 30 minutes at 80°, and then for 60 minutes at 125-130°. Results for the determination of acenaphthylene in synthetic mixtures with acenaphthene are given in Table 1.

Several parallel determinations are given in Table 1 to illustrate the reproducibility of the method. Results of the gravimetric determination of acenaphthylene do not always agree with its actual content in the test mixture, but, thanks to the constancy of the results, which depends on strict observance of the experimental conditions, it is possible to assess the true amount of acenaphthylene on the basis of a calibration curve.

The photometric method is considerably simpler, but it cannot be used directly for the analysis of such a product as that obtained by the dehydrogenation of acenaphthene since this product contains a considerable amount of dark colored, high molecular weight compounds. Vacuum distillation leads to complete removal of the colored compounds which interfere with the determination of acenaphthylene. The speed with which distillation can be carried out, and a high vacuum are of very great importance, in order to avoid resinification and polymerization of the acenaphthylene. Distillation of 20 g of product should not take more than 5-8 minutes, while the residual pressure should not exceed 15 mm. A short-time vacuum distillation is not accompanied by any appreciable resinification of the acenaphthylene. When it is borne in mind that the errors of the methods we have developed for the determination of acenaphthylene lie within the limits of 1%, then it is obvious that the vacuum distillation which precedes determination of the acenaphthylene cannot essentially affect the accuracy of the results.

We have established conditions for the photometric determination of acenaphthylene in the visible part of the spectrum using an ordinary incandescent lamp as the light source. For the visual colorimetric determination of alcoholic solutions of acenaphthylene containing about 0.2 g of this compound in 100 ml of solution, and using a KOL-1 colorimeter with a No. 7 light filter (effective wavelength 449 mμ) the experimental error amounts to 2-3%. For the colorimetric determination of solutions of acenaphthylene containing acenaphthene, it is best to use as a standard reference solution a solution of a mixture of these two compounds containing approximately the same amount of acenaphthylene as the test material. When this is done the experimental error drops and amounts to about 1-2 %.

The best results were obtained when we used the UM-2 universal monochromator with a selenium photoelement. Determinations were carried out at 425 mμ, the thickness of the layer being 20 mm, while the concentration of the acenaphthylene was 0.03-0.04 g in 100 ml of ethanol. In this concentration range the change in optical density of the acenaphthylene solution conforms to Beer's law (see diagram).

As can be seen from Table 2, the experimental error does not exceed 1%.

TABLE 2

Determination of Acenaphthylene in Synthetic Mixtures with Acenaphthene using a UM-2 Monochromator.

Acenaphthylene content of the mixture, %	Acenaphthylene content found,%	Absolute error, %	Acenaphthylene content of the mixture, %	Acenaphthylene content found,%	Absolute error,%
70	69,0	−1,0	87,5	88,2	+0,7
72,5	73,2	+0,2	90	89,7	−0,3
75	75,3	+0,3	92,5	93,6	+1,1
77,5	78,1	+0,6	95	94,8	−0 2
80	79,6	−0,4	97,5	98,0	+0,5
82,5	82.5	0,0	100	99,0	−1,0
85	84,5	−0,5			

SUMMARY

A simple method has been suggested for the isolation of colored and high molecular weight compounds from the crude product obtained by dehydrogenation of acenaphthene. The possibility has been demonstrated of determining acenaphthylene gravimetrically in the form of a sparingly soluble polymer.

A method based on the use of a UM-2 monochromator has been developed for the photometric determination of acenaphthylene in the product obtained by dehydrogenation of acenaphthene.

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* Original Russian pagination. See C.B. Translation.

QUANTITATIVE DETERMINATION OF CYCLOHEXYLNITRITE, CYCLOHEXANONE, AND NITROCYCLOHEXANE IN THEIR MIXTURES

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For the separate determination of cyclohexylnitrite in mixtures,the iodometric method is the form suggested by Beab and Szalkowski [1] for the determination of ethyl- and amylnitrite, was used; the hydroxylamine method [2] was used for the determination of cyclohexanone, while for the determination of nitrocyclohexane a method based on its reduction to the aci-form by means of hydrogen iodide was used [3]. The following original materials were used: cyclohexylnitrite obtained by the action of sodium nitrite on cyclohexanol in an acid medium [4]; commercial cyclohexanol and cyclohexanone; nitrocyclohexane isolated from the appropriate fraction of the nitration products of cyclohexane by dissolving the fraction in 10% NaOH and subsequent precipitation with CO_2. After a two stage distillation, the materials had the following constants: cyclohexylnitrite b.p. 10 mm = 30-32°, n^{20}_{D} 1.4384; cyclohexanone b. p. 760mm= 154-155°, n^{20}_{D} 1.4520; nitrocyclohexane b. p. 40mm = 108-110° n^{20}_{D} = 1.4611; cyclohexanol b. p. 760mm = 160-161°, n^{20}_{D} = 1.4658.

TABLE 1

Compound	Taken, g	Found, %
Cyclohexylnitrite	2,2146	99,7
Ditto	2,5974	99,3
»	2,6155	99,8
Cyclohexylnitrite	0,5485	98,8
Ditto	0,4519	98,6
»	0,4920	97,2
Nitrocyclohexane	1,3106	99,8
Ditto	1,4750	99,5
»	1,0922	99,3

TABLE 2

Mixture	Composition, g	Found, %
Cyclohexylnitrite	2,1617	99,6
Cyclohexanol	2,6470	—
Cyclohexylnitrite	2,4558	99,8
Cyclohexanone	1,0245	—
Cyclohexylnitrite	0,4033	—
Cyclohexanone	0,5028	118,8
Cyclohexylnitrite	2,0348	99,6
Nitrocyclohexane	1,1472	—
Cyclohexylnitrite	1,3960	—
Nitrocyclohexane	1,4312	105,1
Cyclohexanone	0,5410	98,0
Cyclohexanol	1,7320	—
Cyclohexanone	0,4915	97,8
Nitrocyclohexane	0,5240	—
Cyclohexanone	1,0102	—
Nitrocyclohexane	1,2209	99,7
Nitrocyclohexane	1,3111	99,5
Cyclohexanol	1,1520	—

The results given in Table 1 show that the methods chosen give good results for the separate determination of cylohexylnitrite, cyclohexanone, and nitrocyclohexane. It should be borne in mind that the aliquot of cyclohexylnitrite must be dissolved in alcohol immediately prior to determination, since in an alcoholic solution prepared beforehand low boiling ethyl nitrite (+ 17°) is formed as the result of an exchange reaction between alcohol and cyclohexylnitrite, and this can lead to losses when samples are taken.

Cyclohexylnitrite can be determined by the recommended method in the presence of nitrocyclohexane cyclohexanol, and cyclohexanone, but it interferes with the determination of both cyclohexanone and nitrocyclohexane (Table 2). Accordingly, we developed a method for removing cyclohexylnitrite from its mixtures with cyclohexanol and nitrocyclohexane .

Nitrites are known to undergo an exchange reaction withalcohols [5]. Thus, amyl nitrite and propanol react to form propyl nitrite and amyl alcohol. Bearing in mind that methyl nitrite boils at -12°, we made use of the exchange reaction between cyclohexylnitrite and methanol to remove the cyclohexylnitrite:

$$C_6H_{11}ONO + CH_3OH \rightarrow C_6H_{11}OH + CH_3ONO$$

TABLE 3

Test mixture					Found, %			
Taken, g	Content, % wt.				Cyclohexylnitrite	After removal of cyclohexylnitrite		
	methanol	cyclohexylnitrite	cyclohexanone	nitrocyclohexane		cyclohexylnitrite	cyclohexanone	nitrocyclohexane
2,6723	—	100	—	—	99,6	—	—	—
2,1261	—	100	—	—	99,6	—	—	—
8,1511*	75,2	24,2	—	—	40,7	—	—	—
7,2260*	75,2	24,2	—	—	35,5	—	—	—
4,4225**	65,2	23,2	11,6	—	—	Traces	97,8	—
5,0273**	65,2	23,2	11,6	—	—	Ditto	98,6	—
10,5911**	55,2	17,6	9,0	18,2	—	»	97,9	99,8
11,2210**	55,2	17,6	9,0	18,2	—	»	97,7	99,7

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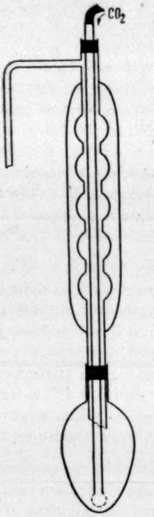
* The mixture of methanol and cyclohexylnitrite was allowed to stand for 15 minutes uncovered prior to analysis. During this stage a considerable part of the cyclohexylnitrite was converted into methyl nitrite and was removed as CH_3ONO.

** The nitrite was decomposed beforehand and the methyl nitrite formed removed.

The exchange reaction does not proceed to completion with higher boiling alcohols. In order to ensure that the reaction goes to completion with methanol, excess of the latter was taken and the methyl nitrite formed removed from solution by passing CO_2 through it. The technique used for removing cyclohexylnitrite is as follows; methanol (2-3 times the amount of nitrite contained in the mixture) is added to the test solution and the solutions obtained placed in the apparatus shown in the diagram. The apparatus is a flask fitted with a reflux condenser. Through the top of the condenser a tube with a perforated enlargement at the end is introduced into the flask; CO_2 (at room temperature) is passed through this tube. The flow of CO_2 is stopped when the issuing gas gives a negative test for nitrite. The test for nitrite is carried out by attaching a test tube containing acidified KI solution to a side tube fused into the top of the condenser. CO_2 is passed through the apparatus for 10-20 minutes. At the end of this period the contents of the flask are analyzed for their content of cyclohexanone and nitrocyclohexane.



It is clear from the results obtained (Table 3) that cyclohexanone and nitrocyclohexane are quantitatively determined after removal of cyclohexylnitrite.

SUMMARY

It has been shown that cyclohexylnitrite can be quantitatively determined in the presence of nitrocyclohexane, cyclohexanol, and cyclohexanone, but the presence of cyclohexylnitrite interferes with the determination of cyclohexanol and nitrocyclohexane. A method has been developed for removing cyclohexylnitrite. It has been shown that after the cyclohexylnitrite has been decomposed, cyclohexanone and nitrocycylohexane can be quantitatively determined: the ketone by the hydroxylamine method, while the nitro compound is determined by its reduction with hydrogen iodide in the alkaline solution.

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THE DETERMINATION OF HALOGEN IN HALOGEN-CONTAINING COMPOUNDS

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The chief problem during the analysis of organic halogen containing compounds is the conversion of the halogen into the ionic state. A number of techniques have been suggested for this purpose: complete decomposition of the material, e.g. by nitric acid (Carius' method) [1] or by combustion in oxygen with subsequent complete oxidation with hydrogen peroxide or with silver salts; splitting off the halogen by the action of alkali or alkali metals [2]; saponification with alkalis in various aqueous and alcoholic media; the action of metallic sodium in various alcohols and neutral solvents [3]; reduction with nascent hydrogen [4], etc. The conditions used for converting the halogen into the ionic state are chosen in accordance with the structure of the molecules of the test halogen compound. The most general method is Carius' method, the complexity of this method, however, prevents its widespread application. Methods based on the action of alkali, and of alkaline metals in solvents, are used more often.

Ruzhentseva and Kolpakova [5] studied a method which they have suggested on a large number of examples. In the present article we should like to point out several facts observed during the analysis of halogen derivatives, in order to show carefully one must proceed in choosing the experimental conditions.

During the determination of chlorine in aliphatic halogen-containing acids (e.g. 7-chloroheptanoic, 9-chlorononanoic), benzal chloride, and cuminal chloride, using reduction with a skeleton nickel catalyst in an alkali solution, of aqueous ethanol , the results proved unsatisfactory. This was difficult to understand because determination of chlorine in such a material as chlorobenzene by the same method gives good results.

It was thought that an increase in temperature would favor the reduction; accordingly we used alcohols with a higher boiling point than ethanol. Isoamyl- and benzyl alcohols, and ethylene glycol were tried. Since heating in isoamyl and benzyl alcohols was accompanied by strong darkening of the solution we chose ethylene glycol.

On boiling the test halogen compound with a skeleton nickel catalyst in an alkaline solution of aqueous ethylene glycol we got satisfactory results (Table 1).

It might be assumed therefore that in the case of the halogen-containing acids which we tested , dehalogenation on boiling with a skeleton nickel catalyst in an alkaline medium, occurs not as a result of reduction with hydrogen contained in the catalyst [6], but as the result of the action of the alkali.

In order to check on this possibility we carried out a series of test in which the halogen-containing acids were boiled with 0.5 N alkali in 50% aqueous ethylene glycol in the absence of the nickel catalyst. Under these conditions, it was found that the test halogen-containing acids were actually dehalogenated quantitatively. Monochloroacetic acid which was analyzed by the authors of the work cited by means of a skeleton nickel catalyst, was quantitatively dehalogenated on boiling with 0.5 N alcoholic potassium hydroxide.

Satisfactory results were also obtained during the determination of chlorine in other materials (Table 2).

Reduction by means of hydrogen is not always superfluous . For example, chlorine in chlorobenzene can be determined with reasonable accuracy only by the method of Ruzhentseva and Kolpakova, or by the Stepanov method which is arbitrarily based on a reduction reaction.

TABLE 1

Acid	Weight taken, g	0.1 N $AgNO_3$ used for titration, ml	Amount of Cl, %		
			calculated	found	found by combustion
5-Chloroheptanoic	0,1430	10,14	26,0	25,3	26,0
9-Chlorononanoic	0,1136	5,85	18,40	19,27	18,21
11-Chloroundecanoic	0,1072	4,87	16,10	16,10	16,3

TABLE 2

Compound	Weight taken, g	0.1 N $AgNO_3$ titer, ml	Amount of Cl, %		
			calculated	found	found by combustion
5-Chloropentanoic acid	0,1390	10,1	26,0	25,8	26,0
7-Chloroheptanoic acid	0.2437	15,0	21,6	21,8	21,9
9-Chlorononanoic acid	0,1627	8,4	18,4	18,3	18,21
11-Chloroundecanoic acid	0,1545	7,04	16,2	16,17	16,3
Benzal chloride	0,0374	4,65	44,09	44,12	44,1
Cuminal chloride	0,0227	2,21	34,9	34,6	34,59
Chloroacetic acid	0,0849	8,52	37,5	35,73	35,86

In the case of halogen determination in halogen acids with an open chain of carbon atoms, it is probably true to say that the reaction is simply one of saponification with alkali which depends on the temperature. There is no simple, universal method, for the determination of halogen-containing compounds.

Chlorine is determined by adding to 0.1 g of test material 4 g of a paste of skeleton nickel catalyst, 25 ml of 0.5 N KOH in ethylene glycol and 15 ml of 10% aqueous NaOH solution. The mixture is boiled under reflux for half an hour on a sand bath. On completion of the reaction the condenser is washed with water, the catalyst filtered and then washed with distilled water until the wash liquors give a negative test for chloride ions (test with $AgNO_3$). The filtrate is acidified with nitric acid and a Volhard titration carried out. A blank is carried out at the same time.

For determination of chlorine in halogen-substituted acids, benzal- and cuminal chloride where no catalyst is needed, the following procedure is adopted: about 0.1 g of test material is placed in a 100-150 ml reaction flask and 20 ml of 1 N NaOH in 50% aqueous ethylene glycol pipetted into the flask. The reaction mixture is heated on a sand bath for 1.5 hours. When the reaction is complete the mixture is neutralized and acidified with nitric acid, and the chlorine determined by a Volhard titration. The results obtained are shown in Table 2.

SUMMARY

Reduction by a skeleton nickel catalyst in an aqueous alcohol medium does not give quantitative results for the determination of chlorine in aliphatic halogen-substituted acids.

It has been shown that in these cases quantitative results can be obtained by using 0.5 N alkali in a high-boiling solvent. The most suitable solvent found was 50% aqueous ethylene glycol.

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MIRRA OSIPOVNA KORSHUN

(1900-1958)

Soviet analytical chemistry has suffered a serious loss: on December 1, 1958 after a serious illness there occurred the death of Mirra Osipovna Korshun a member of the Analytical Commission of the Presidium of the USSR Academy of Sciences, a member of the Commission on Microchemical Methods of the International Union of Pure and Applied Chemistry, and the director of the Laboratory of Microanalysis of the Institute of Heteroorganic Compounds of the USSR Academy of Sciences.M. O. Korshun was a pioneer of organic microanalysis in the Soviet Union. She devoted all her working life to the development of this important branch of chemistry.

Mirra Osipovna Korshun was born on August 21, 1900 in Wilno. She started her working life at an early age as a pharmaceutical student apprentice; her thirst for knowledge led her to undertake hard work in pharmacies and chemical factories. In 1929 she finished her course in the chemical faculty of Moscow State University in the organic chemistry section. At first she worked as a chemist in an industrial laboratory and was appointed leader of the analytical group in 1933. Her work in the field of elemental microanalysis dates from this period.

In 1937 she organized and became head of the laboratory of microanalysis, first in the Institute of Organic Chemistry, then, from 1954, in the Institute of Heteroorganic Compounds of the USSR Academy of Sciences; here she continued as director till her death.

M. O. Korshun became an active propagandist for micromethods of elemental analysis—a field of analytical chemistry which was almost undeveloped at that time in the Soviet Union. Alive to all questions of organic synthesis, M. O. Korshun came to adopt the classical methods of microanalysis. Thanks to her great scientific intuition, her profound knowledge of analytical chemistry, and thanks to her experience coupled with her unusual industriousness M. O. Korshun found her calling in organic analysis. A new, original principle for the rapid pyrolytic combustion of organic materials, in an empty tube in a rapid stream of oxygen, which she has suggested, has proved very fruitful. The wide application of this principle based on an all-round study of the mechanism of pyrolytic combustion, led M. O. Korshun to develop a whole series of so called "rapid methods of microelemental analysis". Using these methods it has proved possible to determine simultaneously three to four elements on one aliquot of material amounting to a few milligrams; thus, it is possible to carry out a simultaneous determination with carbon and hydrogen of such elements as sulfur or halogen; phosphorus, sulfur or halogen; silicon; metal and halogen; metal and sulfur. The principle of preliminary pyrolysis led M. O. Korshun to develop a method for the direct determination of oxygen together with halogen, and also methods for the determination of sulfur and nitrogen by hydrogenation, and nitrogen in a carbon dioxide stream. Rapid methods of analysis include methods for the simultaneous determination of halogens in organic materials after decomposition of the latter with metallic potassium in a bomb; these methods have also been developed by Korshun.

The results of M. O. Korshun's studies have been published in her monograph "New Methods of Elemental Microanalysis", which has already been published in China, and is going to be published in America and England. She has left behind her about 50 scientific papers. Her death interrupted her work on a second, enlarged issue of her monograph.

The success of the new methods and their rapid adoption had a lot to do with the active participation of M. O. Korshun in preparing cadres of qualified microanalysts, in creating a Soviet school of microanalysis and organizing a number of large laboratories (in factory No 51, in the Institute of Organic Chemistry in the Institute of Heteroorganic Compounds of the USSR Academy of Sciences, in the old and new buildings of Moscow State University), and also in guiding standardization, and in introducing microanalytical apparatus and weights into industrial production.

M. O. Korshun's activity was rewarded by the Soviet Government by the award of the Order of the Red Banner of Labor, and by the Badge of Honor and other medals.

In M. O. Korshun we have lost not only a first-rate scientist, and an outstanding organizer, but also a person, liberally endowed with such qualities as a highly developed sense of civic duty and an honest attitude toward work. All these qualitites were combined in M. O. Korshun together with modesty and personal charm. The memory of M. O. Korshun as a fine, cordial person, untiringly serving science in our country will always remain with those who knew her.

THE V. I. VERNADSKII INSTITUTE OF GEOCHEMISTRY AND ANALYTICAL CHEMISTRY OF THE USSR ACADEMY OF SCIENCES INVITES APPLICATIONS FOR ADMISSION TO POSTGRADUATE WORK IN THE SPECIALITIES OF GEOCHEMISTRY AND ANALYTICAL CHEMISTRY

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PRECISION IN SPECTROPHOTOMETRY

COMMUNICATION 1. ERRORS IN SPECTROPHOTOMETRIC MEASUREMENTS

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Measurement of optical density, or, more accurately, determination of the spectrophotometer reading for the test solution, is the final operation in spectrophotometric analysis. In a number of cases, it is precisely this operation that limits the precision of an analysis. The problem we have set ourselves is to consider the sources of error in the measurements of the readings of a photoelectric spectrophotometer, and to show how this error depends on the reading itself.

A number of detailed articles [1-4] have been devoted to this problem. In our work we have not considered systematic errors determined by the non-proportionality of the electric current and the light energy, by the fact that the light is not sufficiently monochromatic, by incorrect calibration of the scale, by difference in absorption and by the length of the cuvette,etc., since these errors do not affect the precision of measurements of the spectrophotometer reading ; but of the optical density. We are concerned not with errors in measuring the optical density (or transmittance) but the errors in reading the spectrophotometer, because an analysis is carried out on the basis of the spectrophotometer readings, which can differ considerably from the true values of the optical density as a result of systematic errors.

In the present article T and D designate, respectively, the readings of the transmittance scale and the optical density scale.

It has been repeatedly pointed out [5-8] that the errors in measuring the readings of the transmittance scale on spectrophotometers with electrical compensation do not depend on the readings of the scale T. It was precisely under this condition that the optimum readings of the spectrophotometer have been determined [5, 7]. Calculation of the errors during setting up of the transmittance scale on 0 and 100 gives only insignificant corrections [2, 9].

Sources of Errors During Measurement of Spectrophotometer Readings

It is necessary to distinguish two independent sources of error in the measurements:

1. The nonreproducibility of the spectrophotometer readings during photometric measurements of the same object (cuvette + solution) in the same position. In this case the error $\sigma_{T_{sp.}}$ (we shall call it the instrumental error) is determined by insufficient sensitivity of the spectrophotometer and the inability of the eye to establish absolutely accurately the position of the pointer on the scale.

2. The nonreproducibility of the cuvette during repeated filling with solution. This error $\sigma_{T_{gk}}$ (cuvette error) is determined by the impossibility of placing the cuvette in exactly the same place, and maintaining constant absorption (as a result of variations in the cleanliness of the cuvette and small corrosion of its surface).

The errors indicated are independent of each other. Accordingly, the dispersion of the total error of measurement is equal to the sum of the dispersion of its components:

$$\sigma_T^2 = \sigma_{T_{sp}}^2 + \sigma_{T_{gk}}^2. \qquad (1)$$

the transmittance scale is expressed by the formula:

$$\sigma_T = \sqrt{\sigma^2_{T_{sp}} + \sigma^2_{T_{gk}}} \tag{2}$$

Let us consider the indicated components of the total error separately.

Spectrophotometer. All these discussions relate to a spectrophotometer with electrical compensation (SF-4 spectrophotometer, Beckman spectrophotometer, etc.). The error in the reading of the transmittance scale σ_T is considered for two reasons: 1) the transmittance scale is uniform; 2) the sensitivity of the spectrophotometer with respect to the transmittance scale is independent of T.

The sensitivity of a spectrophotometer s is equal to the ratio of the deflection of the milliammeter needle from an arbitrary zero (in milliammeter scale divisions) to the shift in the transmittance scale in divisions (1 division corresponds to 1 absolute percent transmittance) causing this deflection ([10], p. 68). For a constant position of the potentiometer, the sensitivity s does not depend on the readings of the transmittance scale; we confirmed this experimentally. Normally, a fairly high sensitivity (greater than 2) is used during measurements. Measurement of the transmittance consists of three independent stages, each of which gives a corresponding error.

A. Setting the Transmittance Scale on Zero (compensation of the dark current). In this case the error is determined by inaccuracy in setting the milliammeter needle on zero because of apparatus instability $\sigma_{(ma)instab.}$ and by inaccuracy in visually determining the position of the milliammeter needle at zero $\sigma_{(ma)vis.}$.

The total error (in milliammeter divisions)

$$\sigma_{(\mu a)} = \sqrt{\sigma^2_{(\mu a)instab} + \sigma^2_{(\mu a)vis}} \tag{3}$$

does not depend on T.

The error determined by inaccurate setting of the milliammeter needle on the zero, in transmittance scale divisions, is expressed by the formula:

$$\sigma_{T\,sens} = \frac{1}{s}\,\sigma_{(mA)} \tag{4}$$

$\sigma_{T_{sens.}}$ only depends on the sensitivity of the spectrophotometer. During measurement of the transmittance T, the error arising from inaccurate setting of the transmittance scale on zero is given by

$$\sigma_{T_0} = (1 - T)\,\sigma_{T_{sens}} \tag{5}$$

since scale T is uniform, while at the point T = 1, the error $\sigma_{T_0} = 0$ (this point is established independently).

B. Setting the Transmittance Scale at 1.0 (with the switch "on"). In this case the error is again only determined by $c_{T_{sens.}}$. The error in measuring the transmittance because of inaccurate setting on 1.0 is given by

$$\sigma_{T_1} = T\sigma_{T\,sens} \tag{6}$$

(at the point T =), the error $\sigma_{T_1} = 0$).

C. Reading the Transmittance T. During reading of T the error not only depends on the inaccuracy of the setting of the milliammeter needle on zero, but also on the error $\sigma_{T_{vis.}}$ of the visual reading of the transmittance scale:

$$\sigma_{T_{read}} = \sqrt{\sigma^2_{T_{sens}} + \sigma^2_{T\,vis}}\,. \tag{7}$$

The total instrumental error during a single measurement of the transmittance of the same photometrically measured object is expressed by the formula:

$$\sigma_{T_{sp}} = \sqrt{\sigma^2_{T_0} + \sigma^2_{T_1} + \sigma^2_{T_{read}}}. \tag{8}$$

Substituting equations (5), (6), and (7), and transforming, we get

$$\sigma_{T_{sp}} = \sqrt{\sigma^2_{T_{vis}} + 2(T^2 - T + 1)\sigma^2_{T_{sens}}}. \tag{9}$$

This formula differs from the equation derived by Gridgeman [2],

$$\sigma_T = \sigma_{T_{read}}\sqrt{2(T^2 - T + 1)}, \tag{10}$$

since Gridgeman expressed the error arising from inaccurate setting at 0 and 1 by the error in reading $\sigma_{T_{read.}}$. This, obviously, is not correct, since it is not taken into account that the error of the visual reading $\sigma_{T_{vis.}}$, which affects the accuracy of taking the readings, does not affect σ_{T_0} and σ_{T_1}, while the error $\sigma_{T_{vis.}}$ is fairly high in comparison with $c_{T_{sens.}}$ when the sensitivity of the apparatus is high. It should be pointed out that Gridgeman, in general, did not analyze the error in taking the reading, which he considered to be independent of T.

Formula (9) shows that $\sigma_{T_{sp.}}$ depends on T to a lesser extent than Gridgeman indicated. It can be shown that at a high sensitivity s (about 2 and higher), when

$$\sigma_{T_{sens}} < \sigma_{T_{vis}}, \tag{11}$$

the instrumental error throughout the whole range of T does not change by more than 8%, i.e., to a certain approximation it can be considered that $\sigma_{T_{sp.}}$ is independent of T. But, even at low sensitivity, (greater than $\sigma_{T_{sens.}}$), the instrumental error only changes by 13%. Accordingly, henceforth we shall consider

$$\sigma_{T_{sp}} = \text{const} \tag{12}$$

(for a constant sensitivity of the apparatus).

The rules governing the choice of spectrophotometer sensitivity will be considered in a separate article.

The error in measuring the readings of the optical density scale is determined by the well known equation

$$\sigma_D = \frac{0{,}43\sigma_T}{T}. \tag{13}$$

This means that

$$\sigma_{D_{sp}} = \frac{0{,}43\sigma_{T_{sp}}}{T}. \tag{14}$$

$\sigma_{D_{sp.}}$ rapidly increases with increasing D (Fig. 1, Curve 1).

Cuvettes. The second source of random errors in measuring the transmittance is the nonreproducibility of the state of the cuvette. Hitherto, the effect of this source of error on the precision of a measurement has not been expressed mathematically.

The transmittance measured is the product of the transmittance of the solution $T_{soln.}$ (with respect to a standard solution) and the transmittances of the cuvette with respect to each other $T_{cuv.}$:

$$T = T_{soln} \cdot T_{cuv} \tag{15}$$

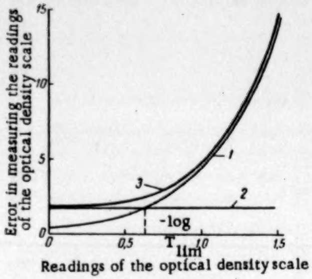

Fig. 1. The error in measuring the readings of the optical density scale: $\sigma_{T_{sp.}} = 1$ (arbitrary), $T_{limit.} = 1/4$ 1) $\sigma_{D_{sp.}}$; 2) $\sigma_{D_{cuv.}}$; 3) σ_D.

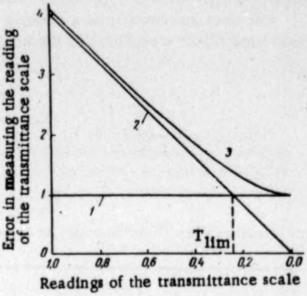

Fig. 2. The error in measuring the readings of the transmittance scale: $\sigma_{T_{sp.}} = 1$ (arbitrary); $T_{limit} = 1/4$; 1) $\sigma_{T_{sp.}}$; 2) $\sigma_{T_{gk}}$; 3) σ_T.

The transmittance of the solution is constant.

The error in the reading of the transmittance scale caused by the nonreproducibility in the state of the cuvette ([11] p. 93) (the index g shows that this is an error in the scale reading, and not an error in measuring the transmittance of the cuvette):

$$\sigma_{T_{gk}} = T_{soln} \cdot \sigma_{T_{cuv}} \tag{16}$$

where $\sigma_{T_{cuv.}}$ is the mean square deviation of the transmittances of the cuvette relative to one another on changing the solution, and is independent of the transmittance of the solution. $T_{cuv.} \approx 1$, and, consequently, [from Formula (15)] $T_{soln.} = T$. Accordingly,

$$\sigma_{T_{gk}} = T \cdot \sigma_{T_{cuv}} \tag{17}$$

Thus, the error in the reading of the transmittance scale caused by the nonreproducibility of the state of the cuvette is strongly dependent on T: it decreases with decreasing T (Fig. 2, Curve 2). At the same time, the corresponding error in the readings of the optical density scale [from Formulas (13) and (17)].

$$\sigma_{D_{gk}} = 0{,}43\,\sigma_{T_{cuv}} = \sigma_{D_{cuv}} \tag{18}$$

does not depend on the readings of the spectrophotometer, and is equal to the mean square deviation of the optical densities of the cuvette relative to each other on changing the solutions.

The Total Error in Measuring the Spectrophotometer Readings

We shall find the total error in measuring the readings on the transmittance scale by substituting equation (17) in Formula (2)

$$\sigma_T = \sqrt{\sigma^2_{T_{sp}} + T^2\sigma^2_{T_{cuv}}} \tag{19}$$

In a similar way, it is possible to find the total error of measuring the reading of the optical density scale (from (13) and (19));

$$\sigma_D = 0{,}43\sqrt{\frac{\sigma^2_{T_{sp}}}{T^2} + \sigma^2_{T_{cuv}}} \tag{20}$$

From equations (19) and (20) it follows that the error in measuring the reading of the spectrophotometer depends on the reading itself (Fig. 1 and 2, Curve 3).

Experimental Verification of the Equation for the Measurement Error on the Spectrophotometer

Special measurements were made on a SF-4 spectrophotometer with the aim of a) demonstrating the reality of the existence of the cuvette error in measurement, b) confirming the theoretical equation derived for the total error of measurement, and c) finding and comparing $\sigma_{T_{sp.}}$ and $\sigma_{T_{cuv.}}$

Six solutions of titanium sulfate with the following concentrations were prepared: 1) 12.0; 2) 13.0; 3) 14.2; 4) 15.9; 5) 19.8, and 6) 31.5 mg of titanium in 100 ml of solution. Each 100 ml of solution also contained 5 ml of 20% hydrogen peroxide, 20 g H_2SO_4, and 0.5-1.0 g of $(NH_4)_2SO_4$. These solutions were photometrically measured with respect to a similar solution of the peroxide complex of titanium with a concentration of 12.0 mg of Ti in 100 ml. The same pair of rectangular cuvettes with a thickness of l = 1.003 cm for the absorbing layer was used. The external optical surfaces of the cuvettes were washed with distilled water and alcohol and then wiped with cambric. When the solutions were changed around the standard solution was changed first. The wavelength of 408 mμ corresponded to the maximum on the absorption curve for the peroxide complex of titanium. The slit width of the monochromator was 0.22 mm (this corresponded to a width of the spectral interval of 2.2 μ). The sensitivity of the apparatus was $s = 2.5$.

In order to exclude the effect of possible changes in the operating conditions of the apparatus with time, the solutions were photometrically measured in a definite sequence (the method of symmetrical observations [10]): solution 1, 2, 3, 4, 5, 6 (first filling of the cuvette); 6, 5, 4, 3, 2, 1 (second filling of the cuvette; 1 . . . 6 (third filling of the cuvette); 6, . . . 1 (fourth filling of the cuvette). In all, each solution was changedfour times, m = 4.

The results obtained were subjected to analysis of variance according to the following scheme.

During photometric measurement (as is usually done in practice) n = 3 single readings of T_i were made, and the mean reading for the i'th filling of the cuvette determined:

$$\overline{T}_i = \frac{\sum_j^n T_j}{n} \tag{21}$$

and the mean dispersion for a single reading calculated

$$s^2_{T_{sp'}} = \frac{\sum_i^m \sum_j^n (T_j - \overline{T}_i)^2}{m(n-1)}. \tag{22}$$

The dispersion of the mean reading which is determined by the instrumental error is n times less:

$$s^2_{T_{sp}} = \frac{s^2_{T_{sp'}}}{n}. \tag{23}$$

Next, the mean reading of the transmittance scale for a given solution was calculated

$$T = \frac{\sum_i^m \overline{T}_i}{m} \tag{24}$$

and the dispersion of the mean reading determined

$$s_T^2 = \frac{\sum\limits_i^m (\overline{T}_i - T)^2}{m - 1} . \tag{25}$$

The second series of measurements was then checked by the same scheme and the corresponding dispersions found.

The use of Cochrane's G criterion ([11] p. 328) (for a significance level of 0.05) showed that the empirical dispersions in both series are estimates of the same general dispersions.

Dispersion of the Measurement Errors

Readings of the transmittance scale	0,99	0,77	0,58	0,40	0,23	0,13
$\sigma_T^2 \cdot 10^6$	25,2	8,4	17,6	5,9	2,0	3,4
$\sigma_{T_{\text{sp.}}}^2 \cdot 10^6$	2,2	2,0	2,1	1,7	0,7	1,5
$\sigma_{T_{\text{gk}}}^2 \cdot 10^6$	23,0	6,4	15,5	4,2	1,3	1,9
$\sigma_{T_{\text{cuv.}}}^2 \cdot 10^6$	23,3	10,9	47,0	26,2	26,0	105,5*

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*Not taken into account during meaning.

In the table is given the mean dispersions for both (k = 2) series for each spectrophotometer reading.

The dispersions s_T^2 and $s_{T_{\text{sp.}}}^2$ for each reading T have the following numbers of degree of freedom, respectively, $N_1 = k(m-1) = 6$ and $N_2 = km(n-1) = 16$. For all readings T, apart from T = 0.13, the ratio $s_T^2 / s_{T_{\text{sp.}}}^2$ exceeds the tabular value of the F-criterion for a significance level of 0.05. At high values of T (0.99; 0.77; 0.58) $s_T^2 / s_{T_{\text{sp.}}}^2$ exceeds even the value of the F-criterion for a significance level of 0.01.

Accordingly, it can be affirmed that, at least for high values of T, changing the solution introduces a considerable error into the mean reading. This is the cuvette error $\sigma_{T_{\text{gk}}}$.

The general dispersions are evaluated empirically as follows:

$$\sigma_T^2 \simeq s_T^2, \ \sigma_{T_{\text{sp}}}^2 \simeq s_{T_{\text{sp}}}^2 \ \text{и} \ \sigma_{T_{\text{gk}}}^2 = \sigma_T^2 - \sigma_{T_{\text{sp}}}^2 \tag{26}$$

Thus, the reality of the existence of the cuvette error is established.

The use of Cochrane's criterion (for a significance level of 0.05) ([11] p. 238) shows that $s_{T_{\text{sp.}}}^2$ obtained at various values of T are estimates of the same general dispersion $\sigma_{T_{\text{sp.}}}^2$.

Thus, the instrumental error can be regarded as being independent of the spectrophotometer reading. The mean dispersion of the instrumental error $\sigma_{T_{\text{sp.}}}^2 = 1.7 \times 10^{-6}$.

Equation (19) shows that there should be a linear relationship between σ_T^2 and T^2. The correlation coefficient of σ_T^2 and T^2 ([12], p. 79), was calculated; r = 0.851 for four degrees of freedom, which exceeds the value of the correlation coefficient for a significance level of 0.05. This indicates that there is a relationship between σ_T^2 and T^2. The equation for the regression line ([12], p. 81) was found in the form

$$\sigma_T^2 = 2{,}9 \cdot 10^{-6} + 20{,}8 \cdot 10^{-6} \cdot T^2. \tag{27}$$

Equation (27) shows that the equation theoretically derived for the error in measuring the readings of the transmittance scale (19) is applicable to the experimental results.

From a comparison of equations (19) and (27) it follows that the coefficients for the equation of the regression line should be considered as $\sigma^2_{T_{sp.}} = 2.9 \times 10^{-6}$ and $\sigma^2_{T_{cuv.}} = 20.8 \times 10^{-6}$.

We found the dispersion of the transmittance of the cuvette with the blank solution directly from our results:

$$\sigma^2_{T_{cuv}} = \frac{\sigma^2_{T_{gk}}}{T^2} \tag{28}$$

From the corresponding dispersions we find the mean square errors $\sigma_{T_{sp.}} = \sqrt{1.7 \cdot 10^{-6}} = 0.13\%$, $\sigma_{T_{cuv.}} = \sqrt{26.7 \cdot 10^{-6}} = 0.52\%$.

Thus, we find that for a fairly high spectrophotometer sensitivity, $\sigma_{T_{cuv.}}$ is considerably (four times) greater than $\sigma_{T_{sp.}}$, i.e., the precision of spectrophotometric analysis is limited by the cuvette error (when the readings of the spectrophotometer D are not very high).

Accordingly, serious attention must be given to the problem of cutting down the cuvette error, thus: a) it is essential to place the cuvette in exactly the same position each time (by means of a special holder) on the same side of the photoelement; b) on changing the solutions the outer optical surfaces of the cuvette should remain clean so that it should not necessary to rinse and wash them (in the course of a given series of measurements of the optical density of samples and standards).

As we have shown [13], an estimate of $\sigma_{T_{sp.}}$ and $\sigma_{T_{cuv.}}$ is necessary in order to determine the optimum scale readings. The most convenient and suitable method of determining $\sigma_{T_{sp.}}$ and $\sigma_{T_{cuv.}}$ is an m-fold (m = 10-20 changes of solution) photometric measurement of the blank solution with n unit readings for each change of solution ($n = 3$). The dispersion of the errors are determined according to formulas (21-26) and (28).

The values we obtained for the errors of measurement cannot be regarded as constants. For example, in one of the determinations of titanium by a differential method (on another SF-4 spectrophotometer) the following values were obtained $\sigma_{T_{sp.}} = 0.04\%$ and $\sigma_{T_{cuv.}} = 0.19\%$ ($\sigma_{T_{cuv.}}/\sigma_{T_{sp.}} = 4.8$). From Bastian's results [14] it follows that in his work the ratio $\sigma_{T_{cuv.}}/\sigma_{T_{sp.}}$ is considerably greater than in our experiments (as a result of a smaller instrumental error).

It must be emphasized that in spectrophotometric work, e.g., [7, 15], the reproducibility of spectrophotometer readings, as a rule, was determined by changing the solutions in the cuvettes several times i.e., an error which includes both the instrumental and the cuvette error was calculated. The cuvette error was not analyzed. Nevertheless, in the literature, as we have noted already, it is always stated that the error in the readings of the transmittance scale is constant. Thus, the constancy of the instrumental error has been extended without any proof to the cuvette error. As pointed out in the present article, this contradicts both theoretical and experimental results.

Limiting (Boundary)—Reading

The equations for the total error in the spectrophotometer readings testify to the fact that when $\sigma_{T_{sp}} < \sigma_{T_{cuv.}}$ (which is usually the case in practice) then at low values of D (high T), the error is determined by the reproducibility of the state of the cuvette (Fig. 1 and 2). On the other hand, for fairly large values of D (small T) the error in the spectrophotometer readings is determined by the instrumental error.

There exists a definite limiting (boundary) value for the scale reading for which both components are equal:

$$\sigma_{T_{gk}} = T\sigma_{T_{cuv}} = \sigma_{T_{sp}}$$

From which

$$T_{\text{lim}} = \frac{\sigma_{T_{\text{sp}}}}{\sigma_{T_{\text{cuv}}}}.$$

It should be remembered that $\sigma_{T_{\text{sp.}}}$ is the instrumental error of the mean reading, which depends on the number n of repeated individual readings.

For a given analysis (constant sensitivity of the spectro photometer, the same number of individual readings, and the same method of treating the cuvette) the limiting reading of the scale is constant.

Introducing the limiting reading of the scale into the equation for the errors of the spectrophotometer readings, we get:

$$\sigma_D = \sigma_{D_{\text{cu}}} \sqrt{1 + \left(\frac{T_{\text{lim}}}{T}\right)^2}, \tag{31}$$

$$\sigma_T = \sigma_{T_{\text{cu}}} \sqrt{T_{\text{lim}}^2 + T^2}, \tag{32}$$

$$\sigma_D = 0,43\sigma_{T_{\text{sp}}} \sqrt{\frac{1}{T_{\text{lim}}^2} + \frac{1}{T^2}}. \tag{33}$$

$$\sigma_T = \sigma_{T_{\text{sp}}} \sqrt{1 + \left(\frac{T}{T_{\text{lim}}}\right)^2}. \tag{34}$$

For $\sigma_{T_{\text{cuv.}}} = 0$, and consequently $T_{\text{limit.}} = \infty$, equations (33) and (34) transform into the well known equations

$$\sigma_D = \frac{0,43\sigma_{T_{\text{sp}}}}{T}, \tag{35}$$

$$\sigma_T = \sigma_{T_{\text{sp}}} = \text{const}. \tag{36}$$

But, as already pointed out, usually $T_{\text{limit.}} = \sigma_{T_{\text{sp.}}}/\sigma_{T_{\text{cuv.}}} < 1$. It can be shown that only for $T \leq 0.46\ T_{\text{limit.}}$, i.e., only for very small T (very large D), is $\sigma_T = \sigma_{T_{\text{sp.}}}$ (with an accuracy of up to 10%) and it can be considered that σ_T = const.

Thus, under normal analytical conditions, i.e., for not very large D, the error in measuring the reading of the transmittance scale cannot be regarded as being independent of the readings. At low D ($T \geq 2.2\ T_{\text{limit.}}$) the error in measuring the reading of the optical density scale can be regarded as constant: $\sigma_D = \sigma_{D_{\text{cuv.}}}$ = const. (with an accuracy of up to 10%).

SUMMARY

The sources of random errors in measurements carried out on an electrically compensated spectrophotometer are considered.

An equation is derived for the errors in spectrophotometric measurements, taking into account the nonreproducibility of the state of the cuvette (purity and position). It has been established that the error in measuring the readings of the transmittance scale depends on the value of the reading.

A study has been made of the reproducibility of measurements carried out on an SF-4 spectrophotometer. It has been shown that the decisive factor affecting the precision of the measurements when using a highly sensitive spectrophotometer is the nonreproducibility of the state of the cuvette.

The equation derived for the errors in measurement has been verified experimentally.

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A STUDY OF THE ERRORS OF X-RAY SPECTROGRAPHIC ANALYSIS

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At present a number of papers are being published on the application of the methods of mathematical statistics for studying the various problems of analytical chemistry [1-6]. The aim of the present work was the use of these methods for a comparative study of the errors of x-ray spectrographic analysis. The study was carried out taking as an example the quantitative x-ray spectrographic determination of Hf and Zr in menerals and the products of technological treatment.

Apparatus and Experimental Procedure

For our work we used a vacuum focusing x-ray spectrograph of the Johann type with an x-ray tube fitted with a tetrahedral anode [7] and operating on the flyback principle [8]. The tetrahedral anode of the x-ray tube could be rotated on a joint around its axis without breaking the vacuum. In order to cut down the background, the anode was made from aluminum. Under the operating conditions of 25 kilowatts, 6 ma, and a 15 minute exposure, the sensitivity for the determination of Hf was 0.01%. For the determination of more than 0.1% and 5% of Hf and Zr respectively, exposure time could be reduced to 6 minutes without any sacrifice of accuracy. A bent quartz crystal with reflecting surfaces $(11\bar{2}0)$ was used. The radius of curvature of the crystal was 500 mm. Zr and Hf were determined quantitatively on the basis of the $K\beta_1$ and $L\beta_1$ lines of these elements respectively in the second and first order of reflection. The technique used in this work differed in this particular respect from that described previously [7]. In order to avoid distortion of the relative intensity of the lines of both elements (the determination of which is of special interest for carrying out geochemical studies), the crystal plus casette was uniformly rocked within the limits of the angles of reflection from 15°30' to 17°. The spectra from the sample located on the four faces of the multifaced anode were recorded on one film. For this purpose, in front of the focal circumference of the casette was fixed a shutter with a slit through which only a fine beam of x-rays containing the β_1 lines of the test elements and the narrow adjoining part of the spectrum could pass. The film was pulled behind the slit in the shutter by means of a SD-2 synchronous motor after expiration of the chosen exposure time.

The cathode of the x-ray tube was provided with a focusing hood in the form of a brass square 10 × 10 mm. Inside the latter were placed two quartz rods with platinum wire 0.5 mm in diameter and 120 mm long wound on them; the wire was covered with an oxide paste of the usual composition. The oxide layer was not renewed more often than after 60-70 hours of operation of the x-ray tube. When the cathode was constructed in this way, the focusing spot was almost a right rectangle with an area of 2 × 3 mm.

The current passed through the x-ray tube was kept constant (with an accuracy of ± 0.5%) by means of a special stabilizer. The high voltage was supplied to the tube from a double semiperiod transformer. The voltage was kept constant by means of a S-96 kilovoltmeter. The vacuum in the apparatus ($2.5\text{-}6 \times 10^{-2}$ mm Hg) and in the x-ray tube ($5\text{-}6 \times 10^{-5}$ mm Hg) was also kept constant, as well as the distance between the anode and the cathode h, and the filament current of the cathode $i_{\text{cath.}}$. The spectrograph case was separated from the x-ray tube. The vacuum was measured separately in the two parts.

The use of aluminum anodes necessitated a change in the method of placing the samples on them. Instead of the usual technique of rubbing the sample into the surface of the anode, the following technique was used. The anode was treated with emery (corundum) paper until an even, roughened surface was obtained. 1-2 mg of test material was then uniformly spread on the anode surface by means of a razor blade, and, using the same razor blade the surface was then covered with a thin layer of BF-2 paste. During the preaging of the tube, before an actual determination, the solvent in the paste evaporates away while the sample on the anode remains covered with a thin film, and, as tests showed, is kept stably in such a position for many hours. The more effective use of the sample, which is ensured by adopting such a technique for applying it to the anode, increases the intensity of the spectral line by approximately 30%. Another advantage of the method (compared with the rubbing technique) is the high degree of uniformity of the layer formed on the anode.

Standards were prepared by careful mechanical grinding of weighed amounts of zirconium and hafnium oxides with the titanium oxide used as a base. The standards contained 0.25, 0.5, 1.0, and 2.5% of hafnium and 20% of zirconium, and were similar in composition to the minerals or rock concentrates which are met in the course of geochemical studies.

Each of the standards was placed on one of the faces of the anode, and, after preaging, was x-rayed under strictly standard conditions; the process was repeated a number of times, and after definite time intervals, on one film. Duro-film was used. Development was carried out in cylindrical tubes, in fresh standard "Rapid" developer for 18 minutes at 18 ± 0.5° in a thermostat. Four spectrograms 15 × 150 mm were developed in each tube. The films were fixed in an acid fixer.

The spectrograms were photometrically measured on a MF-2 photometer with a slit of 130 and a logarithmic scale, all the lines being measured at the same height (1 mm from the lower edge of the spectrum). The blackening of the spectrogram background ($S_{\text{back.}}$) was measured on one side of the line, since interfering lines were located on the other side. The line blackening S_l was calculated by means of the formula $S_l = \Delta S = S_{l+\text{back.}} - S_{\text{back.}}$.

A Statistical Study of the Errors of Quantitative X-Ray Spectrographic Determination of Hf and Zr

The first step in our studies was to verify the hypothesis of normality.* A normal distribution of the analytical results, as one would expect on the basis of the limiting theorem of Lyapunov, should be obtained in those cases where there are no dominating factors among the numerous factors affecting the experimental results. In order to check the normality hypothesis, in analytical practice one often makes a statistical analysis of the results of multiple measurements of the same magnitude. Nevertheless this is not the best method, since the results of such an experiment may be affected by factors which slowly change with time, leading thereby to a shift in the scatter center. Under such conditions, the normality hypothesis may be rejected because of incorrect planning of the experiment. More reliable results can be obtained by a combination of small selections [9-11], where instead of studying the distribution of the random value χ, the law of the distribution of the relative deviation** $\tau = \frac{x_l - \bar{x}}{s\sqrt{\frac{n-1}{n}}}$. is studied. When such a method is used, both the distribution parameters—the mean and dispersion—may have different values for different selections. The theoretical values of the frequencies of the τ-distribution are tabulated in [9]. 216 measurements were used (72 selections, each of which consisted of three determinations). The results are presented in Table 1. The group interval is given in the first column, while the second column contains the theoretically expected absolute frequency ν_l° of the appearance of the value τ included in the limits of the interval indicated; the third column contains the frequency actually observed ν_l. Finally, the last column of the Table contains the calculated weighed sum of squares for each of the series of independent determinations $\chi^2 = \sum \frac{(\nu_l - \nu_l^{\circ})^2}{\nu_l^{\circ}}$, these are compared with the tabulated values of the χ^2 distribution [10]. As is evident,

$P(\chi^2 > \chi^2_{\text{expt.}}) = 0.3$, which therefore confirms the normality hypothesis.

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* During the application of mathematical statistics to new test materials it is always advisable to start with verication of the hypothesis of normality; this facilitates further statistical analysis.

** In this article, in accordance with accepted tradition, S^2 denotes the selected dispersion and σ^2 the general dispersion.

TABLE 1

Checking the Normality Hypothesis for Reproducibility Errors

Group intervals		Theoretically expected freq. accord. to[9](ν_i^0)	Freq. observed experimentally (ν_1)	$(\nu_i - \nu_i^0)^2/\nu_i^0$
Positive deviations	0,0—0,3	4,90	5	0,002
	0,3—0,6	5,16	6	0,144
	0,6—0,9	5,76	9	1,823
	0,9—1,2	7,41	7	0,022
	1,2—1,5	12,79	18	2,122
Negative deviations	0,0—0,3	4,90	6	0,246
	0,3—0,6	5,16	5	0,004
	0,6—0,9	5,76	5	0,100
	0,9—1,2	7,41	1	5,520
	1,2—1,5	12,79	10	0,605
	Sum	72	72	10,588

Note: The number of degrees of freedom f = 10-1 = 9, $P(\chi^2 > \chi^2_{\text{expt.}}) \simeq 0.3$.

The verification of the normality hypothesis described, only relates to intralaboratory reproducibility errors. It was also of interest to check this hypothesis for errors characterizing the deviation between the results of determinations obtained by chemical and spectrographic methods. For this purpose we treated the results of 48 parallel chemical and x-ray spectrographic determinations. The results are illustrated in Table 2. The first column contains the group intervals expressed in parts of σ; the second column contains the absolute frequency expected on the basis of a normal distribution (ν_i^0); while the last column contains the experimentally observed frequencies (ν_i), and the values of $(\nu_i - \nu_i^0)^2/\nu_i^0$ calculated for them. A comparison of the experimental results with the theoretically calculated frequencies indicates that the distribution studied is near to normal. The fact that the normality hypothesis is valid allows one to use analysis of variance for investigating the errors of x-ray spectrographic determinations. In the first instance it is reasonable to resolve the total experimental error into two values; the reproducibility error $\sigma_{\text{reprod.}}$ characterizing the scatter of the experimental results with respect to the mean obtained during a short time interval, and σ_T the error determined by other factors. For this purpose the results of 20 determinations for each of four standards (three in parallel) were treated; all were taken on one plate. The results of the experiments for each of the standards were arranged as shown in Table 3. Here the scatter along

TABLE 2

Verification of the Normality Hypothesis for Errors Characterizing the Deviation between the Results of X-Ray Spectrographic and Chemical Analysis

Group intervals	Theoretically expected frequency ν_i^0	Experimentally observed frequency ν_i	$(\nu_i - \nu_i^0)^2/\nu_i^0$
0.0-0.67	23.8	27	0.43
0.67-1.0	8.8	6	0.89
1.0-1.4	7.5	6	0.30
1.4-2.0	7.9	9	0.15
Sum	48	48	1.77

Note: The number of degrees of freedom f = 4-2 = 2; $P(\chi^2 > \chi^2_{\text{expt.}}) \simeq 0.4$.

TABLE 3

Arrangement of Material during a Study of the Dispersion Determined by the Effect of One Factor

Parallel determinations	Films		
	1	2 . . .	20
First	x_{11}	x_{21}	x_{201}
Second	x_{12}	x_{22}	x_{202}
Third	x_{13}	x_{23}	x_{203}

the columns is determined by the reproducibility error $\sigma_{\text{reprod.}}$ in experiments separated by small time intervals, while the vacuum of the apparatus remains unchanged, and the apparatus works under constant conditions and the same conditions are used for developing the spectrograms; $\sigma_{\text{reprod.}}$ does not depend on the conditions used for securing the sample to the anode of the x-ray tube. The factors which have the greatest effect on this error are the nonuniformity of the focusing spot, and the extent of its shift along the anode surface with an unevenly deposited sample, and also errors introduced into the experimental results during photometric determinations of the spectrograms. The scatter between the columns σ_T in Table 3 is caused by other factors. It may depend on errors arising because of some variation in the vacuum and on other parameters which affect the operation of the spectrograph, and on imperfections and differences in the conditions of attaching the test material to the anode of the x-ray tube and on differences in the conditions under which the spectrograms are developed. The dispersion was calculated by means of well known formulas [5]; results of these calculations are given in Table 4. It was established that $\sigma_{\text{reprod.}}$ and σ_T depend on the concentration of the test element (Figs. 1 and 2).

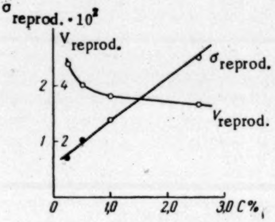

Fig. 1. Relations between the values of $\sigma_{\text{reprod.}}$ (1) and $v_{\text{reprod.}}$ (2) and the concentration of the test element.

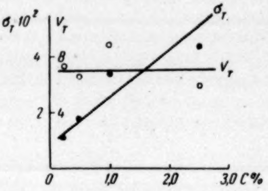

Fig. 2. Relations between the values of σ_T (1) and v_T and the concentration of the test element.

As for the variation coefficients V_{VT} and V_{VT} (the relative errors of the measurements), in view of the fact that for x-ray spectrographic determinations the following relation holds

$$\log \Delta S = a + b \log C$$

these can be calculated by means of the formula

$$v = \frac{\sigma_c}{C}\% = \frac{\sigma_{\Delta S}}{b \cdot \Delta S} \cdot 100,$$

they are almost constant for all the tested range of changes in concentration of the elements, and are equal, on an average, to 3.9 and 7.1% respectively (Table 4).

TABLE 4

The Square Errors and Variation Coefficients during Hafnium Determination

C, %	$\overline{\Delta S}$	$\sigma_{\text{reprod.}} \times 10^2$	$\sigma_T \cdot 10^2$	$V_{\text{reprod.}}$ %	V_T, %
0.25	0.123	0.71	1.09	4.7	7.2
0.50	0.225	1.02	1.69	4.0	6.6
1.00	0.334	1.37	3.36	3.6	8.8
2.50	0.652	2.47	4.36	3.3	5.9

An attempt was made to resolve the error σ_T into two values: σ_{RT}. the error determined by the instability of the processes of rubbing the standard on the anode and σ_T, the error determined by the remaining factors which are not controlled and which change slowly with time. Experiments were carried out so that four standards containing the same amount of Zr were rubbed into the four different faces of the anode. 12 spectra were photographed on each film (4 standards in triplicate). In the course of 1.5 months 20 films were prepared containing 240 spectrograms altogether. The experimental results were presented in the form of a two stage group as shown in Table 5. Analysis of variance* showed (Table 6) that σ_{RT} and $\sigma_{T'}$ differ significantly from zero. Calculations led to the following results.

$$\sigma_{rep} = 1{,}05 \cdot 10^{-2} \quad V_{rep} = 3{,}2\%$$
$$\sigma_{RT} = 1{,}53 \cdot 10^{-2} \quad V_{RT} = 4{,}6 \,.$$
$$\sigma_{T'} = 2{,}02 \cdot 10^{-2} \quad V_{T'} = 6{,}1 \,.$$

TABLE 5

Arrangement of Material During a Study of Dispersion Determined by the Action of Two Factors

Parallel determinations	Plates		
	1 . . . 20		
	Rubbing 1 . . . 4	. . . . .	Rubbing 1 . . . 4
First	x_{111} . . . . . x_{141}	. . . . . .	x_{2011} . . . . x_{2041}
Second	x_{112} . . . x_{142}	. . . . . .	x_{2012} . . . . x_{2042}
Third	x_{113} . . . x_{143}	. . . . . .	x_{2013} . . . . x_{2043}

Thus, the results of an analysis of variance show that in the general balance of errors, in addition to the rubbing process (which obviously needs improving) other uncontrolled factors play a large part. In this connection there arises the necessity of clarifying the question of the expediency of increasing the number of controlled factors, and applying the necessary corrections for such factors.

First, attention was given to the development process. Variations in the temperature and duration of the development of the spectrograms (using a standard developer) have an appreciable affect on the position of the calibration curves. For example, on changing the duration of development (Fig. 3) there is observed a parallel shift of the curves. This is reflected in the absence of correlation between the values X and Y (Fig. 4) determined by the method of least squares in the equation

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*For a detailed description of the analysis of variance for a two stage classification see, e.g., [12].

$$\Delta S = X + YC,$$

by means of which it is possible to represent (Fig. 3, below) the relation between the blackening of the x-ray lines of hafnium and its concentration in a sample for a narrow concentration range.

TABLE 6

Results of Analysis of Variance Obtained during a Study of Errors Arising during Determination of Zirconium

Origin of the dispersion	No. of degrees of freedom	Sum of squares	Mean sum of squares	F
Plates obtained at different times (factors which change slowly with time)	20-1 = 19	788.15	41.48	3.1*
Rubbing	20 (4-1) = 60	799.83	13.33	12.1**
Reproducibility	80(3-1) = 160	176	1.10	–
Sum	239	–	–	–

*Significant for a significance level of 0.001

** The same for << 0.001.

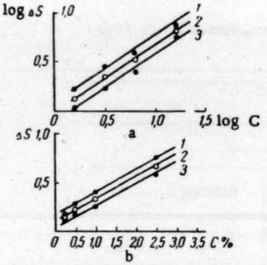

Fig. 3. Calibration curves for the x-ray spectrographic determination of Hf in a sample, and the relation between their position and the duration of development 1) 10 minutes; 2) 8 minutes; 3) 6 minutes.

Neither was any correlation established between the values of X and Y and changes in the most important parameters characterizing the conditions under which the spectrograph operates—the strength of the filament current $i_{\text{cath.}}$, the pressure p in the apparatus, and the distance h between anode and cathode. The results given graphically in Figs. 5-9 testify to this. Worthy of attention is the fact that the parameter X (Fig. 5a, 6a, 7, 8, and 9) varies within fairly wide limits (from 0.07 to 0.14), while the slope of the calibration curve—parameter Y (Fig. 5b, 6b, 7, 8, 9) remains almost unchanged (about 1.13).

Thus, it seems that there is no need to apply corrections for changes in the filament current, and for changes in the pressure, and the distance between the anode and cathode. At the same time there occurs a parallel shift in the calibration curves, which is, presumably, caused by some instability in the development process. From a practical point of view it must be acknowledged that it is necessary to use one standard for controlling the position of the calibration curve, although this precaution leads to an increase in the duration of a determination.

The precision of the determination of the mean value $\overline{\Delta S}$ both for the control standard, and for the test sample is calculated by the formula:

$$\sigma_{\overline{\Delta S}} = \sqrt{\sigma_r^2/nm + \sigma_{rt}^2/m},$$

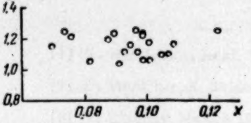

Fig. 4. Verification of the hypothesis regarding the correlation between the parameters of the calibration curve.

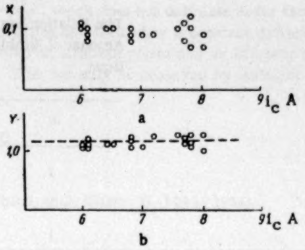

Fig. 5. Verification of the hypothesis of a link between parameters X (a) and Y (b) and changes in the filament current of the cathode $i_{\text{cath.}}$.

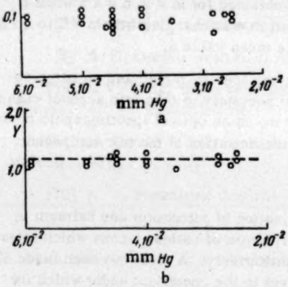

Fig. 6. Verification of the hypothesis of a relation between the parameters X (a) and Y (b) and changes in the vacuum of the spectrograph.

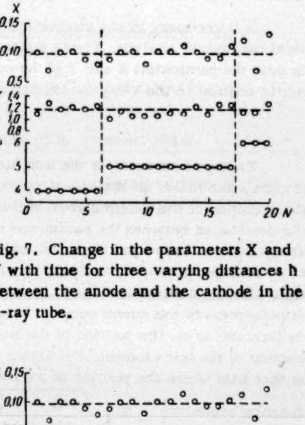

Fig. 7. Change in the parameters X and Y with time for three varying distances h between the anode and the cathode in the x-ray tube.

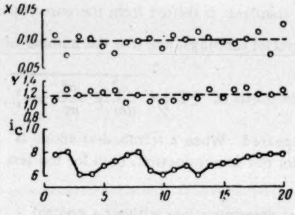

Fig. 8. Verification of the hypothesis of a relation between the parameters X and Y and changes in the strength of the filament current of the cathode with time.

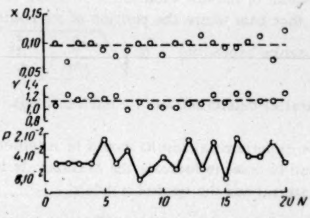

Fig. 9. Verification of the hypothesis of a relation between the parameters X and Y and changes in the vacuum in the spectrograph with time.

TABLE 7

The Relation between the Errors in Determining $\overline{\Delta S}$ and the Amount of Rubbing and the Number of Parallel Determinations

m	n	$\sigma_{\overline{\Delta S}} \cdot 10^{-2}$
1	1	1.85
1	2	1.70
1	3	1.65
2	1	1.51
2	2	1.31
2	3	1.24

where m is the number of parallel rubbings (applications), and n is the number of parallel determinations for each rubbing. In Table 7 are given the results of calculating $\sigma_{\overline{\Delta s}}$ for various values of m and n. The numbers obtained show that on using a tetrahedral anode, the optimum precision is obtained for m = 2, n = 2* when it is necessaery to photograph the standard and sample simultaneously. When m = 1, changing from n = 2 to n =3 has almost no effect on increasing the precision of the determination of the mean value S.

It is necessary to pay attention to the essential difference between x-ray spectrographic and emission optical methods of analysis. For an optical method, in the general case, it is necessary to take into account changes in both the parameters X and Y of the curves. The values of $\sigma_{\text{reprod.}}$ and σ_T in an optical spectrographic method, in contrast to the x-ray spectrographic method, do not depend on the concentration of the test component.

SUMMARY

Taking as an example the quantitative x-ray spectrographic determination of zirconium and hafnium in minerals and rocks, an analysis of variance of the errors has been made. The role of various factors which affect the precision of the determination of the elements has been evaluated quantitatively. A study has been made of the correlation between the parameters of the calibration curves and changes in the conditions under which the analysis is conducted and the conditions used for developing the spectrograms. It has been shown that, in contrast to optical spectrographic analysis, for which, in the general case, it is necessary to take into account changes with time of both parameters of the calibration curve, in the case of x-ray spectrographic analysis only mutual parallel displacement of the curves occurs. This makes it possible to carry out a determination on the basis of one constant calibration curve, the position of the latter being controlled by means of only one standard with not a very small content of the test element. For known values of $\sigma_{\text{reprod.}}$, σ_{RT}, and σ_T' the basic curve should only be shifted in that case where the position of the points corresponding to the control standard is shifted from the curve by a distance exceeding $\pm 2\sqrt{\frac{\sigma_r^2}{nm}+\frac{\sigma_{rt}^2}{m}}$ (where m is the number of parallel rubbings, and n is the number of parallel determinations for each rubbing). When this shift lies outside the limits of $\pm 2\sqrt{\frac{\sigma_r^2}{nm}+\frac{\sigma_{rt}^2}{m}+\sigma_T^2}$, the experimental results should be regarded as incorrect and should be repeated. When a tetrahedral anode is used in order to increase the accuracy, it is best to choose m = 2, n = 2 for the determination, both for the test material and the control standard.

When one constant calibration curve is used for carrying out express determinations without a control standard, increasing the number of photographs for one rubbing should have little effect on the experimental results, since its error to a large extent depends on the value of $\sigma^2_{RT} + \sigma^2_{T}'$, which does not decrease under these conditions. It should also be borne in mind that the experimental precision obtained when a constant calibration curve is used, which has been obtained by meaning experimental results on different plates and at different times, cannot be increased by periodically checking the calibration curve. This can only be achieved by taking spectrograms on the same plate as that used for the control standard.

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*Even greater possibilities are opened up by further increasing the number of faces on the anode.

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THERMOSPECTROPHOTOMETRIC DETERMINATION OF THE RARE EARTH ELEMENTS IN THE PRESENCE OF THORIUM

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The photometric determination of thorium in fairly acid solutions against a background of the rare earths can be carried out without any difficulty. Determination of the rare earths in the presence of thorium is, however, difficult. It is necessary, first of all, to separate thorium, using well known techniques [1-9], or to carry out two determinations of the light absorption at different pH values and determine the rare earths by difference [6, 10]. The latter method has, of course, limited application, and for low rare earth contents gives inaccurate results, or may be inapplicable altogether.* As far as we are aware there are no direct chemical methods for the determination of the rare earths against a background of thorium. Such determinations become possible on using a new technique which we have called thermophotometry.

By thermophotometry or thermospectrophotometry we designate the technique whereby spectrophotometric determinations are carried out at two different temperatures. If the solution contains only two elements, and if, on changing the temperature, the light absorption of the complexes of these elements changes to a different extent, then having obtained two values of the optical density at the different temperatures, the content of each element can be determined by solving a system of two simultaneous equations with two unknowns. In individual cases this general method can be essentially simplified. The essence of this phenomenon has already been described earlier [11].

The effect of pH on the intensity of the color of solutions of the complex compounds formed by reagents of the type R-OH, is shown in the general form in Fig. 1. Curves of this type are observed for all temperatures. Under such conditions, the higher the temperature, the more is the curve displaced to the acid side**. The decrease in the color intensity on increasing the pH to a value greater than that corresponding to maximum development of the color, is probably connected not with decomposition of the complexes as is sometimes assumed, but with a decrease in the intermolecular dissociation of these cyclic complexes, which is also responsible for the colors observed [12]. On heating a solution of the complex having a pH lying on the ascending branch of the curve (Fig. 1, a), the color intensity of the solution will increase. When the pH corresponds to a point lying on the descending branch of the curve (Fig. 1, b), the color intensity, will on the other hand, in hot solutions be lower than in cold solutions. At a pH corresponding to the point of intersection of the curves (Fig. 1, c) the intensity of the color of a solution of the complex (but not the intensity of the color of excess colored reagent present) will be the same at those temperatures for which the curves were constructed. At other temperatures the curves will intersect at another point.

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*The possibility is indicated in the article by Kuteinikov and Lansky [10] of photometric determinations of the rare earths on a background of thorium by difference. However, these authors do not give details of a method or of any results they may have obtained.

**As a consequence of additional reasons not considered here, the descending branch of the curve corresponding to the higher temperature is not always shown up so clearly and correctly as shown in Fig. 1.

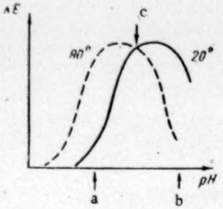


Fig. 1. Relation between the light absorption of a solution of the complex an and pH at 20 and 80° (scheme)

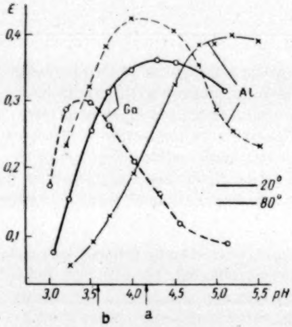


Fig. 2. Effect of temperature on the light absorption of solutions of the complexes of Al and Ga with arsenazo on changing the pH. Concentrations in mole liter; Al 0.00025; Ga 0.00050; arsenazo 0.00050. Cuvette length 40 mm. λ = 576 mμ.

When the cations of two elements which hydrolyze with varying ease are present in solution, the optimum conditions for color development of their complexes will be found at different pH. On comparing the curves for two elements, as is shown for the case of compounds of Al and Ga with arsenazo in Fig. 2, it is clear that at the pH corresponding to point a, heating will increase the intensity of the color of the Al complex and simultaneously weaken the intensity of the color of the Ga complex. At a pH corresponding to point b, the increase in the color intensity will be proportional to the concentration of the Al complex, since the intensity of the color of the Ga complex at this pH will not change with changes in temperature.

The same is true of a mixture of two other cations which hydrolyze at different pH's, i.e., cations whose hydrocomplexes of the type $Me(OH)^{n+}$ have different instability constants. The values of these constants can be found in the monograph by Yatsimirsky and Vasil'ev [13].

If it were necessary to determine an element with readily hydrolyzable cations on the background of an element with cations which hydrolyze with difficulty, e.g., Th on a background of La, such a determination could be carried out without any difficulty. It is simply necessary to work at as low a pH as possible when the element whose cations hydrolyze with difficulty does not react. Thermophotometry is also interesting in that it permits solution of problems which the techniques of ordinary photometry cannot solve. For example, it is possible to determine In on a background of Ga, although Ga^{3+} cations hydrolyze more readily than In^{3+}. Similarly, it is possible to determine Al on a background of In, Al on a background of Ga, etc. Arsenazo (benzene-2-arsonic acid -< 1-azo-7> > -1, 8-dihydroxynaphthalene-3, 6- disulfonic acid) is suitable for this purpose. For determination of Al on a background of Th, the reagent benzene-4-sulfonic acid < 1-azo-2 > , 1, 8-dihydroxynapthalene-3, 6-disulfonic acid etc., is suitable.

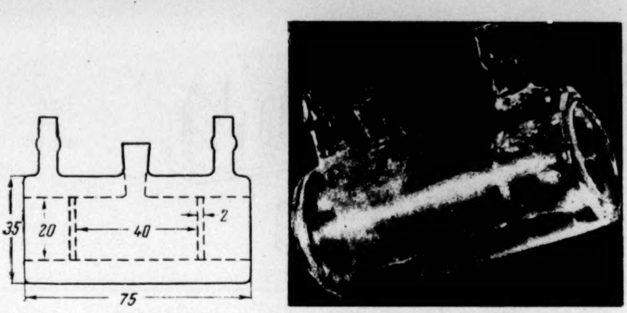
Apparatus

For thermophotometric determinations it is necessary to make measurements of the light absorption at two different temperatures. Of numerous known setups [14-19] which enable the solutions which are being examined to be thermostatted, we chose a quartz cuvette with a jacket (Fig. 3).

A cuvette made from plexiglass can be used. In such a case, however, one cannot work at temperatures higher than 80°. There also arise difficulties associated with getting rid of bubbles of air which adhere to the inner walls of the cuvette during the process of heating the solutions.

Water from Heppler thermostats operating at 20 and 80°, and which can be fairly accurately maintained within ± 0.1-0.2°, is passed into the jacket of the cuvette. Changes in temperature are made by switching over from one thermostat to another by means of taps (screw clips) a and b shown in Fig. 4.

Since the solutions obtained possess too high an optical density, their light absorption should be measured against a grey filter; an uniformly exposed photographic plate with a light absorption of about 3.0 units of optical density is suitable for such a filter.



a b

Fig. 3. Cell fitted with a water jacket

During the experimental work the slit width should be kept constant for construction of the calibration curves and for actual determinations.

Thermospectrophotometric Determination of the Rare Earths in the Presence of Thorium. Arsenazo (benzene-2-arsonic acid-< 1-azo-7 > -1, 8-dihydroxy naphthalene-3, 6-disulfonic acid) is suitable for this purpose; the color reaction of this reagent with the rare earths [20] and its use for the determination of thorium [21, 22] have been described earlier. Arsenazo solutions are rose in color: with Th and the rare earths it forms soluble complex compounds with a violet color.

In Figs. 5 and 6 is shown the effect of pH on the color intensity of solutions of the complex compounds of thorium and mixtures of the rare earths at 20 and 80°.

On heating the solution from 20 to 80° the color intensity of a solution of the thorium complex at a pH of 3.6-3.8 changes little, while the color intensity of solutions of the rare earth complexes at a pH of 3.7 increases 1.9 times for La, about 2.9 times for Yb, and about 2.9 times* for mixtures with the composition we used.

On adding this mixture of rare earths to thorium nitrate free from rare earths, and working at a pH of 3.7, we constructed a calibration curve (Fig. 7). Then, using this curve, the rare earth content of thorium nitrate to which a mixture of rare earths of the same composition had been added, was determined. The results obtained show clearly (Table 1) how the experimental accuracy can be increased by taking the mean of five determinations.

Experimental Procedure. The method is designed for the analysis of separate mixtures of thorium and rare earths. All other elements apart from the alkali metals should be absent. Masking anions which complex Th and the rare earths should also be absent.

The standard nitric acid solution of the nitrates of the rare earths contains 1.0 mg/ liter of total rare earths. The most suitable mixture is one which has a similar composition to the test mixture. In order to prepare it, an accurate aliquot of the calcined oxides (about 0.1 g) is dissolved in HNO_3 and the solution evaporated on a water bath to dryness; the residue is dissolved in water and the volume made up to 100 ml with water. 1.00 ml of this solution is then diluted with water to 100 ml (10γ /ml of total rare earths).

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* A mixture of the rare earths of the yttrium group was used. The composition of the mixture as determined x-ray spectrophotometrically was as follows (% wt.).

Lu	0,75	Ho	1,9	Tb	0,5	Nd	0,9
Yb	6,8	Y	57,0	Gd	1,8	Ge	1,5
Er	7,5	Dy	6,3	Sm	0,3	La	0,75

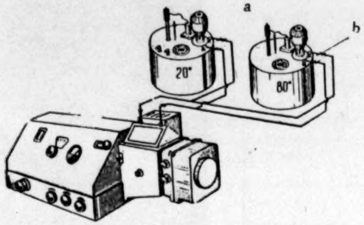

Fig. 4. Schematic diagram of the setup used for thermospectrophotometric determinations.

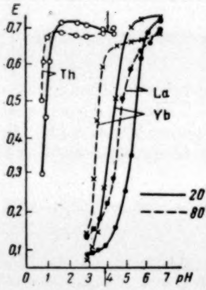

Fig. 5. Effect of temperature on the light absorption of solutions of the complexes of thorium and the rare earths with change in pH. The reagent was arsenazo; λ = 576 mμ; cuvette length 40 mm.

The solution of thorium nitrate in 0.5 N HNO_3 containing about 10 mg/ml of ThO_2 is prepared as follows. About 1 g of $Th(NO_3)_4 \cdot 4H_2O$ free from the rare earths* is dissolved in 50 ml of 0.5 N HNO_3 and the thorium concentration determined gravimetrically.

A buffer solution with a pH of 3.7 is prepared by dissolving 4.72 g of monochloroacetic acid in 10 ml of water and adding, with mixing, in small portions, 21.8 ml of 2.0 N NaOH, and the volume made up to 50 ml. The buffer solution with pH 2.0 is prepared by dissolving 4.72 g of monochloroacetic acid in 10 ml of water and adding, with mixing, 6.12 ml of 2.0 N NaOH and making the solution up to 50 ml.

Construction of a Calibration Curve. Into five 25 ml standard flasks are introduced aliquots of the thorium nitrate solution containing 0.23 mg of ThO_2, and aliquots of the solution of the mixture of rare earths containing 0.000; 0.005, 0.010; 0.020; 0.040 mg of the elements calculated in terms of total oxides; the volume is made up to about 5 ml, and 2 drops of 0.1% phenolphthalein solution added, the mixture is titrated with 0.1 N NaOH until a red color is obtained, the color is destroyed by addition of two drops of 0.05 N HCl. Another 0.016 ml of 0.05 N HCl is added and 8.0 ml of 0.3% aqueous arsenazo solution added, this is followed by addition of 0.4 ml (not more) of the buffer mixture with pH 3.7 and the volume made up to the mark with water. The solutions which are thoroughly mixed are photometrically measured at 20 and 80° in a cuvette with a layer thickness of 40 mm, using a constant slit width of 0.6 mm at a wave length of 576 mμ. The difference between the light absorption of solutions at 80 and 20° is used for constructing the calibration curve.

Analytical Procedure. When solid nitrates or chlorides are analyzed, an aliquot of the preparation corresponding to 10 mg of total oxides of the elements is dissolved in 0.1 N HNO_3 in 100 ml standard flask.

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* When the thorium nitrate contains rare earth elements they are removed by extraction of the thorium nitrate with methyl ethyl ketone [6]. To 1 g of thorium nitrate is added 2 ml of concentrated HNO_3 and the mixture dissolved in 50 ml of water. 75 g of solid ammonium nitrate is added and the solution obtained extracted with an equal volume of methyl ethyl ketone. The ketone extract is washed 3 times with half its volume of a 60% solution of ammonium nitrate acidified with nitric acid. The thorium nitrate is reextracted from the separated ketone phase with 50 ml of 0.1 N HNO_3. After the thorium concentration of the reextract has been determined it is used for the work.

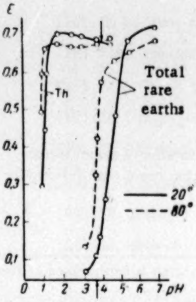

Fig. 6. Effect of temperature on the light absorption of complexes of thorium and the mixture of rare earths used with changes in pH. Reagent–arsenazo; λ = 576 mμ; cuvette length 40 mm. The curves were obtained with solutions of the following concentrations arsenazo 5 × 10^{-4} mole; Th 1.9 × 10^{-4} M and a mixture of the rare earths with a concentration of 1.8 × 10^{-4} M.

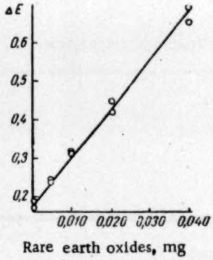

Fig. 7. Calibration curve for the determination of total rare earths in the presence of Th. Reagent–arsenazo; λ = 576 mμ; cuvette length 40 mm.

Thermospectrophotometric Determination of Total Rare Earths in the Presence of Thorium. (Thorium concentration in terms of the oxide 0.23 mg ThO_2 in 25 ml).

Rare earths, in terms of the oxides			Relative error, %
taken		γ in 25 ml found	
rare earth oxides in the total oxides, %	γ in 25 ml		
1,16	3,0	3,6	+20,0
1,16	3,0	2,8	− 6,7
1,16	3,0	3,5	+16.7
1,16	3,0	3,4	+13,3
1,16	3,0	2,5	−16,7
	Mean	3,2	+ 6,7
1,92	5,0	5.4	+ 8,0
1,92	5,0	4,9	− 2,0
1,92	5,0	5,3	+ 6,0
1,92	5,0	5,5	+10,0
1,92	5,0	4,5	−10,0
	Mean	5,1	+ 2,0
3,77	10,0	10,3	+ 3,0
3,77	10,0	10,7	+ 7,0
3,77	10,0	9,4	− 6,0
	Mean	10,1	+ 1,0
5,56	15,0	15,4	+ 2,7
5,56	15,0	14,2	− 5,3
	Mean	14,8	− 1,3
14,89	35,0	36,2	+ 3.4
14,89	35,0	34,3	− 2,0
	Mean	35,3	+ 0,9

During the analysis of precipitated oxalates, the latter together with the filter are transferred to a 100 ml quartz beaker and 10 ml each of concentrated hydrochloric, perchloric, and nitric acid added; the beaker is covered with a cover glass and the mixture heated, first on a sand bath until the filter has decomposed, and then, after removing the cover glass, on an air bath* until white fumes cease to come off. The residue is dissolved in 10 ml of 1 N HNO_3 and the solution transferred to a 100 ml standard flask, the cover glass is rinsed with water and the volume made up to 100 ml.

In order to assess the thorium concentration, 1.00 ml of the solution thus obtained is transferred to a 25 ml flask and about 5 ml of water added, followed by 2 drops of 0.1% phenolphthalein solution, 0.1 N NaOH is added until a red color is obtained which is destroyed by addition of 0.1 N HCl. Another 2 ml of 0.1 N HCl is added, this is followed by 4.0 ml of 0.3% arsenazo solution, 2 ml of the buffer mixture with a pH of 2.0 and the volume made up to the mark with water. The solution is photometrically measured against a solution of the reagent in a 10 mm cuvette at 576 mμ; the concentration of the thorium in the solution in the 100 ml flask is finally calculated by means of the formula:

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*An air bath constructed as follows is suitable: an asbestos grid is placed 7 cm above a 600 watt electric hot plate supplied at a voltage of 220 volts.

$$C_{Th} = E/3{,}70 \text{ mg/ml ThO}_2$$

(E is the light absorption of the solution).

The coefficient 3.7 corresponds to the light absorption given by 1.00 mg ThO_2 in 25 ml.

In order to determine the concentration of the rare earths, an aliquot of the test solution is taken which contains 0.23 mg of ThO_2, and the procedure outlined for the construction of a calibration curve then followed. Three to five determinations are carried out and the mean value taken.

SUMMARY

Thermospectrophotometry is the term given to the technique in which light absorption is determined at two different temperatures.

The reagent arsenazo forms soluble complex compounds with thorium and with the rare earths, and the violet colors of solutions of these complexes behave differently at different pH on heating. On changing the temperature of a solution with a pH of 3.7 from 20 to 80°, the optical density at 576 mμ of the thorium complex does not change, while that of the complex of the rare earths increases by 1.9 (La) to 2.9 (Yb) times. By using a calibration curve and carrying out photometric determinations at 20 and 80°, it is possible to determine the content of rare earths in thorium preparations, starting at a concentration of 1.2% of the rare earths in terms of their oxides. For 1.2% of the rare earth oxides in ThO_2 the experimental error is 7%, while for 15% of the rare earth oxides the error is 1%.

The apparatus and analytical procedure used are described.

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INVESTIGATION OF COMPLEX FORMATION IN SOLUTION BY THE PARTITION METHOD. THE SYSTEM SELENOYL-2-ACETONE-Th (IV)$-CHCl_3-H_2O$

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The partition method (or extraction method) which has been successfully developed in recent years by a number of research workers [1-4] is being widely used for studying the physicochemical characteristics of various complex compounds. By means of this method the instability constants and partition coefficients of the complexes of many metals both with organic and inorganic addenda, have been determined [5-10, 12] in various two phase systems. The work described here is devoted to the study of complex formation of thorium with selenoyl-2-acetone using chloroform as the organic solvent. The values of the dissociation constants and the partition coefficient of selenoyl-2-acetone in the systems $CHCl_3-H_2O$ and $C_6H_6-H_2O$, necessary for calculating the characteristics of the complex formation process, were established previously [11].

All the experiments on the study of the partition of thorium between the organic and aqueous phases were carried out at an initial concentration of thorium in the aqueous phase of 1.0×10^{-6} g. ion/liter, a temperature of 25 ± 0.1° and an ionic strength of 0.1. The radioactive isotope Th^{234}, which was isolated from uranyl nitrate by ether extraction, was used for the work. Selenoyl-2-acetone was synthesized and purified as described earlier [11]; the preparation obtained was kept in a desiccator until its weight was constant. In order to prepare solutions of the reagent, aliquots of the latter were dissolved in a known volume of chloroform or benzene. The organic solvents were carefully purified and their purity controlled by determining their refractive indices ($n_D^{20} = 1.5013$ for C_6H_6 and $n_D^{20} = 1.4468$ for $CHCl_3$). In its remaining details the method did not differ from that described earlier [12]. It was established beforehand that in the absence of selenoyl-2-acetone in the $CHCl_3$ layer, thorium is not extracted from the aqueous phase. A series of experiments were carried out at an original concentration of thorium in the aqueous phase of 9.0×10^{-6} g. ion/liter. The near agreement of the values for the partition coefficients, obtained at concentrations of 1.0×10^{-6} and 9.0×10^{-6} g. ion/liter in the original aqueous solution, testifies to the absence of multinuclear complexes, hydrolysis products, and other polymerized particles, within the concentration range of Th^{4+} chosen [2]. The results of our experiments are in complete agreement with those described earlier for the system 2-hydroxy-1, 4-naphthoquinone$-Th^{4+}-CHCl_3-H_2O$ [12].

In order to establish the composition of the complexes formed in the aqueous phase, partition curves* were taken for thorium selenoyl-2-acetonate at three successively decreasing concentrations of the reagent in the $CHCl_3$ layer. It is known [2] that the partition curves for the metal between the phases log q = f (pH) and log q = f (log-$[HA][H+]^{-1}$) have a different but completely definite shape in accordance with the type of complex formed. The values obtained for the partition coefficients of thorium at concentrations of selenoyl -2-acetone in the $CHCl_3$ layer of 4×10^{-2} M, 1.0×10^{-1}, and 4.0×10^{-1} M are shown in Table 1. The curves relating log q to pH and log $[HA][H^+]^{-1}$ (Figs. 1 and 2 respectively) are in complete agreement with theoretical considerations for complexes of the type $MA_n^{(N-n)+}$(N is the charge on the metal ion). In order to establish the possibility of the

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[*] Henceforth the following designations are used: HA for the molecule of the organic reagent; A for the addendum; pA the reciprocal logarithm of the concentration of free addenda and $q = \Sigma[M]_{organic}/\Sigma[M]_{aqueous}$ is the partition coefficient of the metal.

TABLE 1

Partition of Th^{4+} in the System $CHCl_3-H_2O$ for Various Concentrations of the Reagent in the $CHCl_3$ layer ($t = 25 \pm 0.1°$, $\mu = 0.1$)

$[HA]^{\bullet}_{org.} - 4{,}0 \cdot 10^{-3}$ M				$[HA]^{\bullet}_{org.} - 1{,}0 \cdot 10^{-1}$ M				$[HA]^{\bullet}_{org.} - 4{,}0 \cdot 10^{-1}$ M			
pH	I_{H_2O} imp/min	I_{CHCl_3} imp/min	log q	pH	I_{H_2O} imp/min	I_{CHCl_3} imp/min	log q	pH	I_{H_2O} imp/min	I_{CHCl_3} imp/min	log q
2,40	2235	30	—1,87	2,30	2430	60	—1,61	2,40	795	1582	+0,30
2,70	1200	45	—1,43	2,40	1710	75	—1,36	2,62	219	2271	+1,01
3,50	120	465	+0,59	2,80	930	450	—0,32	2,70	195	2340	+1,08
3,60	120	622	+0,72	3,00	285	465	+0,21	2,90	132	2536	+1,28
3,70	75	870	+1,06	3,30	135	1200	+0,95	3,00	102	2667	+1,42
3,90	45	1230	+1,44	3,40	90	1305	+1,08	3,12	30	2689	+1,95
4,00	14	1200	21,90	3,50	105	1350	+1,09	3,25	21	2641	+2.10
				3,65	60	1665	+1,44	3,55	7	2814	+2,60

TABLE 2

Partition of Thorium in the Systems $CHCl_3-H_2O$ and $C_6H_6-H_2O$

$CHCl_3-H_2O$				$C_6H_6-H_2O$			
pH	I_{H_2O} imp/min	I_{CHCl_3} imp/min	log q	pH	I_{H_2O} imp/min	I_{CHCl_3} imp/min	log q
2,40	2235	30	—1,87	2,40	1500	24	—1,80
2,70	1200	45	—1,43	2,75	851	135	—0,80
3,50	120	465	+0,59	2,80	841	172	—0,68
3,60	120	622	+0,72	3,05	366	292	—0,10
3,70	75	870	+1,06	3,10	331	252	—0,11
3,90	45	1230	+1,44	3,36	78	544	+0,84
4,00	15	1200	+1,90	3,40	75	570	+0,88
				3,70	30	900	+1,48

formation of complexes containing molecules of the organic solvents used, curves were obtained relating the partition coefficient of selenoyl-2-acetone to the pH in the systems $CHCl_3-H_2O$, and $C_6H_6-H_2O$ for an equal concentration of the reagent in the aqueous phase. It has been established [2] that in those complexes into whose composition molecules of chloroform or benzene or another organic solvent do not enter, the curves log q = f (pH) for the condition indicated above $[HA]_{aq.}$ = const, are almost parallel. The vertical distances between curves of this type, which are numerically equal to the ratio of the corresponding partition coefficients, are almost constant throughout the whole pH range studied. The values obtained for the partition coefficients of thorium at various pH's for the system $CHCl_3-H_2O$ and $C_6H_6-H_2O$ are given in Table 2 and in Fig. 3.

The nature of the curves obtained corresponds to the case of complexes which do not contain molecules of benzene or chloroform. Thus, it can be regarded as established that under the conditions chosen, only uninuclear complexes $ThAn_n^{(4-n)+}$, which do not contain molecules of chloroform or benzene, are formed. The general relation between the partition coefficient q and the concentration of free addendum, according to Rydberg [1, 2], is established by the equation :

$$q = -\frac{\lambda_4' \cdot \varkappa_4 [A]^4}{\sum\limits_{n=0}^{n=N} \varkappa_n [A]^n}, \qquad (1)$$

where λ_4' is the partition coefficient of ThA_4, $\varkappa_n$ is the general constant of complexity, N is the maximum number of addenda which can combine with the Th^{4+} ions. The concentration of the free addendum is calculated by

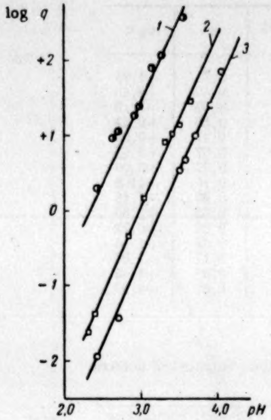

Fig. 1. Partition of Th^{4+} in the system $CHCl_3-H_2O$ as a function of the pH at various concentrations of selenoyl-2-acetone: 1) $[HA]^o_{org.} = 4.0 \times 10^{-1}$ M; 2) $[HA]^o_{org.} = 1.0 \times 10^{-1}$ M; 3) $[HA]^o_{org.} = 4.0 \times 10^{-2}$ M.

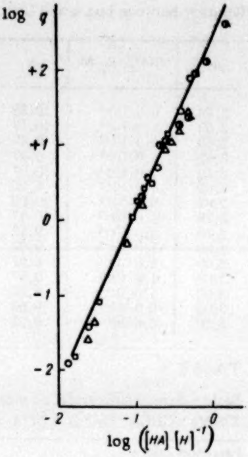

Fig. 2. Partition of Th^{4+} in the system $CHCl_3-H_2O$ as a function of log $[HA][H^+]^{-1}$ at various concentrations of selenoyl-2-acetone: ○) $[HA]^o_{org.} = 4.0 \times 10^{-2}$ M; □) $[HA]^o_{org.} = 6.6 \times 10^{-2}$ M; △) $[HA]^o_{org.} = 1.0 \times 10^{-1}$ M; ◐) $[HA]^o_{org.} = 4.0 \times 10^{-1}$ M.

by means of formula (2):

$$-\log[A] = pA = pK_{dis.} + \log[H^+] - \log[HA]\log + \\ + \lg(K_{par.} + 1 + K_{dis.}[H^+]^{-1}). \qquad (2)$$

where $K_{dissoc.}$ is the dissociation constant of selenoyl 1-2-acetone, $K_{partit.}$ is the partition coefficient of the latter in the system $CHCl_3-H_2O$, $[HA]_{total}$ is the concentration of the reagent in the original solution, $[H^+]$ is the hydrogen ion concentration in the aqueous phase; $pK_{dissoc.} = -\log K_{dissoc.}$. The values of $K_{dissoc.}$ and $K_{partit.}$ were determined earlier [11] and are equal to respectively: $K_{dissoc.} = 2.82 \times 10^{-9}$ and $K_{partit.} = 839 \pm 9$. By introducing into equation (1) the auxiliary constant φ_n

$$\varphi_{4-n} = \frac{[ThA_n][A]^{4-n}}{[ThA_4]} = \varkappa_n \varkappa_4^{-1}, \qquad (3)$$

equation (1) can be represented in the form of a function F_n which enables one to calculate φ_n, and then the general $\varkappa_n$, and the successive k_n complexity constants by means of techniques similar to the method of Leden[13]:

$$F_0 = \frac{1}{q} = (1 + \varphi_1[A]^{-1} + \varphi_2[A]^{-2} + \varphi_3[A]^{-3} + \varphi_4[A]^{-4})\cdot\lambda_4'^{-1}; \qquad (4)$$

$$F_1 = \left(\frac{\lambda_4'}{q} - 1\right)[A] = \varphi_1 + \varphi_2[A]^{-1} + \varphi_3[A]^{-2} + \varphi_4[A]^{-3}; \qquad (5)$$

TABLE 3

Relation between Log q and Concentration of Selenoyl-2-acetone in the Aqueous Phase

pH	$[HA]^{\bullet}_{CHCl_3}$, M	pA	log q	pH	$[HA]^{\bullet}_{CHCl_3}$, M	pA	log q
2,32	$6.6\cdot10^{-2}$	10,33	−1,84	3,12	$4,0\cdot10^{-1}$	8,75	+1,95
2,30	$1,0\cdot10^{-1}$	10,17	−1,61	3,20	$6,6\cdot10^{-2}$	9,45	+0,45
2,40	$4,0\cdot10^{-2}$	10,47	−1,87	3,25	$4,0\cdot10^{-1}$	8,62	+2,10
2,40	$4,0\cdot10^{-1}$	9,47	+0,30	3,30	$6,6\cdot10^{-2}$	9,35	+0,49
2,40	$1,0\cdot10^{-1}$	10,07	−1,36	3,30	$1,0\cdot10^{-1}$	9,17	+0,95
2,62	$4,0\cdot10^{-1}$	9,25	+1,01	3,40	$1,0\cdot10^{-1}$	9,07	+1,09
2,62	$6,6\cdot10^{-2}$	10,03	−1,10	3,50	$4,0\cdot10^{-2}$	9,37	+0,59
2,70	$4,0\cdot10^{-2}$	10,17	−1,43	3,50	$6,6\cdot10^{-2}$	9,15	+1,08
2,70	$4,0\cdot10^{-1}$	9,17	+1,08	3,50	$1,0\cdot10^{-1}$	8,97	+1,18
2,80	$1,0\cdot10^{-1}$	9,67	−0,32	3,55	$4,0\cdot10^{-1}$	8,32	+2,60
2,90	$4,0\cdot10^{-1}$	8,97	+1,28	3,60	$4,0\cdot10^{-2}$	9,27	+0,72
3,00	$1,0\cdot10^{-1}$	9,47	+0,21	3,65	$1,0\cdot10^{-1}$	8,82	+1,44
3,00	$4,0\cdot10^{-1}$	8,87	+1,42	3,70	$4,0\cdot10^{-2}$	9,17	+1,06
3,05	$6,6\cdot10^{-2}$	9,60	+0,05	3,90	$4,0\cdot10^{-2}$	8,97	+1,44
3,10	$6,6\cdot10^{-2}$	9,55	+0,26	4,00	$4,0\cdot10^{-2}$	8,87	+1,90

TABLE 4

Basic Characteristics of Complex Formation Processes in the System Selenoyl-2-acetone Th(IV) · $CHCl_3-H_2O$ (t = 25° ± 0.1°, μ = 0.1)

Partition coefficient of ThA_4	Auxiliary constants φ_n	Successive complexity constants	General complexity constants
$\lambda'_4=556\pm21$	$\varphi_1=1,4\pm0,1\cdot10^{-9}$ $\varphi_2=1,7\pm0,1\cdot10^{-18}$ $\varphi_3=1,7\pm0,1\cdot10^{-27}$ $\varphi_4=1,5\pm0,1\cdot10^{-37}$	$\kappa_1=1,1\pm0,1\cdot10^{10}$ $\kappa_2=1,0\pm0,1\cdot10^{9}$ $\kappa_3=8,0\pm0,6\cdot10^{8}$ $\kappa_4=7,1\pm0,5\cdot10^{8}$	$\varkappa_1=1,1\cdot10^{10}$ $\varkappa_2-1,1\cdot10^{19}$ $\varkappa_3=8,8\cdot10^{27}$ $\varkappa_4=6,6\cdot10^{36}$

$$F_2=\left(\frac{\lambda'_4}{q}-1\right)[A]^4=\varphi_4+\varphi_3[A]+\varphi_2[A]^2+\varphi_1[A]^3. \qquad (6)$$

The experimental values we obtained for log q at various values of pA are given in Table 3; the corresponding partition curve used for successive calculations of function F_n is shown in Fig. 4.

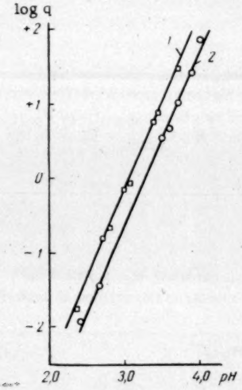

Fig. 3. Partition of thorium in the systems $C_6H_6-H_2O$ (1) and $CHCl_3-H_2O$ (2).

The curve for the function F_0 is shown in Fig. 5. Curves for successive F_n functions are not given, since they are similar in nature to F_0, while their values are readily calculated by means of equations (5-6). The method of deriving the auxiliary constants is exactly similar to that described previously [12]. The values which we found for the constant φ_n, and the successive and general constants of complexity, and also the partition coefficients of thorium selenoyl-2-acetonate in the system $CHCl_3-H_2O$ are given in Table 4.

The values obtained for the characteristics of the process of complex formation in the system examined were used for calculating the percentage distribution of thorium between complexes of various composition as a function of the same value. The corresponding curves are shown in Fig. 6a and 6b.

Thorium selenoyl-2-acetonate, in its physicochemical characteristics essentially differs from the complex compounds of Th^{4+} with other reagents containing groups with identical reactivity. A comparison of the complexity constants obtained for thorium selenoyl-2-acetonate with those determined

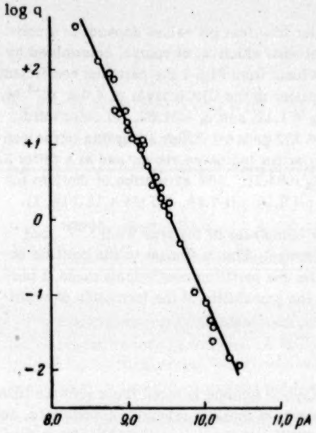

Fig. 4. Partition curve for Th^{4+} in the system $CHCl_3-H_2O$.

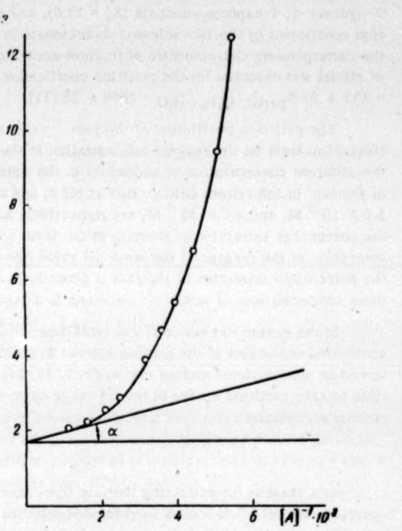

Fig. 5. Curve for function F_0.

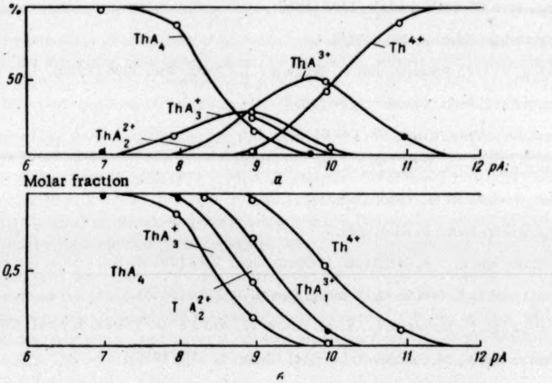

Fig. 6. Percentage distribution of thorium between complexes of differing composition (a), and the molar fraction of the various complexes (b) as a function of the concentration of the free addendum.

earlier for the acetylacetonate [14] and 2-hydroxy-1, 4-naphthoquinonate complexes [12], indicate that the former have a considerably higher stability (the general complexity constants κ_4 are respectively equal to $6.6 \cdot 10^{36}$, $1.0 \cdot 10^{27}$ and $1.5 \cdot 10^{16}$). The partition coefficient of thorium selenoyl-2-acetonate in the system $CHCl_3-H_2O$ ($\lambda_4' = 556$) is considerably higher than the partition coefficient, in the same system, of both the

2-hydroxy-1, 4-naphthoquinonate (λ'_4 = 13.6), and acetylacetonate (λ'_4 = 350 ± 20) of thorium [15]. The partition coefficient of thorium selenoyl-2-acetonate in the system $CHCl_3-H_2O$ (Fig. 3) and is somewhat higher than the corresponding characteristic of thorium acetylacetonate (for the latter λ'_4 in C_6H_6 = 320 [14]). A similar state of affairs was observed for the partition coefficients of the reagent itself in the same systems $K_{\text{partit. } CHCl_3-H_2O} = 839 \pm 9$; $K_{\text{partit. } C_6H_6-H_2O} = 1009 \pm 23$ [11].

The partition coefficient of thorium selenoyl-2-acetonate under identical pH values depends to a considerable extent on the reagent concentration in the layer of organic solvent, which is, of course, determined by the different concentration of addendum in the aqueous phase. As is evident from Fig. 1 the partition coefficients of thorium in the system $CHCl_3-H_2O$ at pH 3, and at reagent concentrations in the $CHCl_3$ layer of 4.0×10^{-2} M, 1.0×10^{-1} M, and 4.0×10^{-1} M, are respectively equal to $q_1 = 0.22$, $q_2 = 1.12$, and $q_3 = 31.62$. In other words the percentage extraction of thorium in the layer of organic solvent $E = 100\, q/1 + q$ differs according to the concentration of the reagent at the same pH value (for the reagent concentrations indicated above, and at a pH of 3, the percentage extraction of thorium is given by $E_1 = 17.2$, $E_2 = 52.8$, $E_3 = 94.7$). 99% extraction of thorium for these concentrations of selenoyl-2-acetone is obtained respectively at pH 3.20, pH 3.85, and pH 4.15 (Fig. 1).

In the system examined it was established that only mononuclear complexes of the type $ThA^{(4-n)+}$, not containing molecules of the organic solvent in their composition, are formed. This is similar to the position observed in other systems studied earlier [1, 2, 12, 14]. The high values for the partition coefficients made it possible to take partition curves in the pH range up to 4, which decreased the probability of the formation of multinuclear complexes.

SUMMARY

As a reagent for extracting thorium from aqueous solutions, selenoyl-2-acetone is much more suitable than acetylacetone which is widely used for this purpose. The stability constants of thorium selenoyl-2-acetonate, and the partition coefficient of the complex being extracted in the system $CHCl_3-H_2O$, are considerably higher than the corresponding characteristics of the acetylacetonate complexes of the element indicated.

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THE EFFECT OF ORGANIC SOLVENTS ON THE CHROMATOGRAPHIC SEPARATION OF Li^+, Na^+, AND K^+ IONS ON SULFORESINS

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The chromatographic separation of the alkali elements in aqueous solutions has been dealt with in a number of papers by foreign workers. A fairly complete review of the literature on this question has been given in the article by Shchipakina, Nemirovskaya, and Senyavin [1]. The authors of this article were unable to achieve quantitative separation of sodium and potassium on the sulforesins SBS, SDV-1, and KU-2.

Most of the work carried out hitherto has been devoted to the separation of sodium and potassium on the sulforesins IR-100, Dowex-50. Jentzsch and Frotscher [2] obtained the best results, but their method requires 24 hours to separate a mixture containing 6 mg · equivalents each of LiCl, NaCl, and KCl on a meter long column of Wofatite KPS.

It has been shown in a series of papers [3-7] that the nature of the solvent in which the ion exchange reaction takes place has a considerable effect on the value of the exchange equilibrium constant.

During a systematic study of the effect of methanol and acetone on the exchange equilibrium of the ions Li^+, Na^+, and K^+ on the H-form of various sulforesins, we showed [8, 9] that with increasing concentration of the organic solvent, the difference in the values of the equilibrium constants increases. This led us to the idea of using mixed aqueous-organic solvents for improving the chromatographic separation of the ions.

Only two papers have been published on the separation of the alkaline elements in aqueous-organic solutions, these are: the paper by Okuno, Honda, and Ishimoru [10] who obtained fair results during the separation of Li^+, Na^+, and K^+ on amberlite-120 in 20-30% methanol; while the other paper is that by Davies and Owen [11]; using a meter long column of Zeokarb-225 they obtained good separation of a mixture containing 1 mg · equivalent each of LiCl, NaCl, and KCl, on eluting the column with a 0.7 N solution of HCl in 80% acetone. Nevertheless, one separation by their method takes about 100 hours.

The aims of the work described here were: to study the chromatographic separation of the alkali elements on sulforesins, to establish the effect of the addition of organic solvents on the separation, and to choose the optimum conditions for separating sodium and potassium, and mixtures of lithium, sodium, and potassium. Of the greatest interest was separation in mixed solvents, in that concentration range of the organic solvent (60-80%), within which the equilibrium constants of the exchange of the separated ions for hydrogen differ most.

The work was carried out on industrial samples of the cation exchange resins Espatite-1, KU-2, and SDV-3. The particle diameter was 0.25-0.5 mm for the first two resins, and 0.10-0.25 mm for SDV-3. Columns 15 mm in diameter but of varying lengths were used.

Before commencing an experiment, the column containing the resin in the H-form was washed with the solvent which was to be used for the work. A mixture of 1 N solutions of the chlorides of the cations to be separated was then introduced into the top of the column. The acid liberated was washed out with the appropriate solvent (this is essential when the analysis is based on change in acid concentration), after which the cations were eluted with a solution of HCl in this solvent. The eluates issuing from the column were then collected in separate

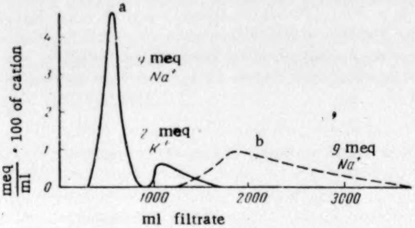

Fig. 1. Separation of sodium and potassium on Espatite; by eluting with 0.1 N HCl. a) Solvent—water, rate at which acid is passed through—3.9 ml/minute; b) solvent—60% acetone, rate at which acid is passed through—5.3 ml/minute.

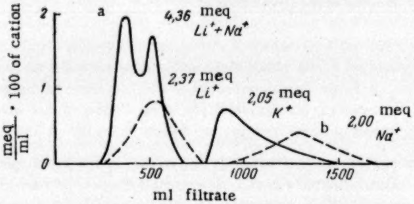

Fig. 2. Separation of lithium, sodium, and potassium on Espatite by eluting with 0.1 N HCl. a) Solvent—water, rate at which acid is passed through—0.7 ml/minute; b) solvent—60% methanol, rate at which acid is passed through—0.7 ml/minute.

fractions of 10-70 ml each. The elution was controlled by means of a spectroscope and by means of the color of a flame. The amount of the metal ions was determined either by the change in the concentration of the acid issuing from the column, or by evaporating the fractions to dryness and titrating the chloride with silver nitrate, using fluorescein as an indicator. Both methods gave results in agreement with each other.

Separation of Na^+ and K^+ on Espatite. A mixture of NaCl and KCl containing 11 mg · equivalents was poured into a column containing 36 g of Espatite. Preliminary tests showed that in order to separate the zones during elution of the cations with 0.1 N aqueous HCl, the optimum rate for passing through the acid was of the order of 5-6 ml/minute. Eluting at a higher rate does not lead to separation. Dropping the rate from 5.4 to 1.2 ml/minute improves the separation and decreases zone merging somewhat, but separation takes much longer.

In Fig. 1 are shown the results of experiments on separating 9 mg · equivalents of sodium and 2 mg · equivalents of potassium in water and 60% acetone. In an aqueous acetone solution it was possible to achieve quantitative separation of sodium from potassium, since Na^+ was eluted with 0.1 N HCl in 60% acetone solution, while K^+ was not detected even after 1000 ml of eluate had been collected. Similar results were obtained for other ratios of sodium to potassium.

Separation of Mixtures of Li^+, Na^+, and K^+ on Espatite. Into a column of the same dimensions as that used in the previous tests was poured a mixture consisting of 2.39 mg · equivalents of LiCl and 2 mg · equivalents each of NaCl and KCl. The column was washed either with an aqueous or an aqueous alcohol solution of HCl. Some of the results are given in Fig. 2. It was found that in water the lithium and sodium zones overlap considerably. The use of a 60% methanol solution made it possible to separate the given mixture quantitatively, the intermediate eluate between lithium and sodium was greater than 100 ml, potassium was not eluted with 0.1 N aqueous alcoholic hydrochloric acid. Increasing the rate at which acid was poured through the column from 0.7 to 2.2

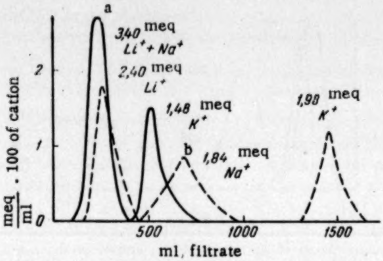

Fig. 3. Separation of lithium, sodium, and potassium on Espatite by eluting with 0.28 N HCl. a) 1.9 mg · equivalents LiCl, 1.5 mg · equivalents NaCl, and 1.5 mg · equivalents KCl; solvent—water; rate at which acid passes through —1.2 ml/minute; b) 2.4 mg · equivalents LiCl, 1.9 mg · equivalents NaCl, and 2.0 mg · equivalents KCl; solvent—60% methanol, rate at which acid is passed through—1.3 ml/minute.

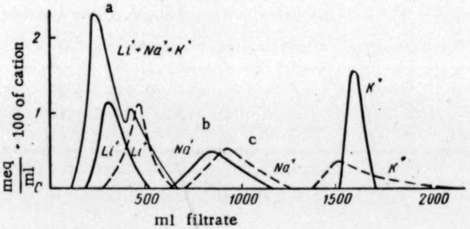

Fig. 4. Separation of a mixture of 1.8 mg · equivalents of LiCl, 1.5 mg · equivalents NaCl, and 1.5 mg · equivalents KCl on SDV-3 by eluting with 0.1 N HCl. a) Solvent—water; rate at which acid is passed through—1.5 ml/minute, b) solvent—60% methanol, rate at which acid is passed through 2.5 ml/minute; c) solvent—60% acetone, rate at which acid is passed through—1.4 ml/minute.

ml/minute did not lead to a deterioration of the separation. In this case, however, the zones were somewhat more diffuse, but the volume of intermediate eluate between Li^+ and Na^+ did not change. In order to reduce the time required it is more convenient to accelerate elution.

In the experiment described, separation demanded a fairly long time. Accordingly, in our subsequent experiments we used a more concentrated acid for eluting (Fig. 3).

On using 0.28 N hydrochloric acid in 60% methanol (Fig. 3b) the zones of lithium and sodium hardly overlapped at all, and, after eluting the sodium, potassium was absent in at least the next 300 ml of eluate (K^+ was eluted here, as in similar cases, with 0.3 N aqueous HCl). In aqueous media, on using 0.28 N HCl, even when smaller amounts of the cations were used (Fig. 3a) Li^+ and Na^+ were eluted together and the interval between Na^+ and K^+ dropped to only 15 ml. Thus, by using Espatite, it is fairly easy to separate, in many cases, sodium and potassium, while by means of a 0.1 N solution of HCl in 60% methanol it is possible to carry out a quantitative separation of lithium, sodium, and potassium.

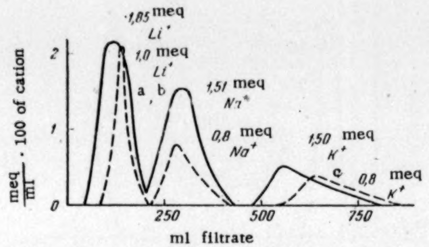

Fig. 5. Separation of lithium, sodium, and potassium on SDV-3 by eluting with 0.28 N HCl in 60% methanol. a) 1.9 mg · equivalents LiCl, 1.5 mg · equivalents NaCl, and 1.5 mg · equivalents KCl, rate at which acid is passed through—0.8 ml/minute; b) 1.9 mg · equivalents LiCl, 1.5 mg · equivalents NaCl, and 1.5 mg · · equivalents KCl, rate at which acid is passed through -2.4 ml/minute; c) 1.0 mg · equivalents LiCl, 0.8 mg · equivalents NaCl, and 0.8 mg · equivalents KCl, rate at which acid is passed through —1.4 ml/minute.

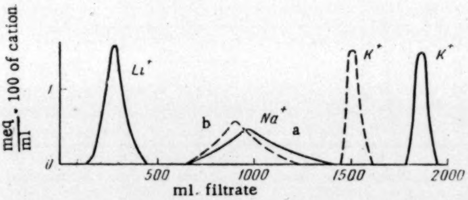

Fig. 6. Separation of a mixture of 1.9 mg · equivalents LiCl, 1.5 mg · equivalents NaCl, and 1.5 mg · equivalents KCl on SDV-3 in 80% methanol. a) Elution with 0.12 N HCl at the rate of 3.5 ml/minute; b) elution rate—5.4 ml/minute. Initial HCl concentration—0.12 N; after 660 ml of eluate had been collected 0.24 N HCl was used, while after 1450 ml of eluate, 0.6 N HCl was used.

Separation of Na^+ and K^+ on KU-2. The exchange equilibrium constants for the ions to be separated on the H-form of the cation exchange resin KU-2 are respectively 1.49 and 2.34 for water, and 8.42 and 16.70 for 60% methanol (the method used for determining these values has been described earlier [3]). Accordingly, one should expect here again that there will be an improvement in the separation on using 60% methanol.

During the separation of a mixture of 3 mg · equivalents NaCl and 1 or 2 mg · equivalents of KCl on a column 20 cm long and containing 12 g resin, and using 0.1 N aqueous HCl, the sodium and potassium zones did not overlap, although the interval between them was not very large. The use of 60% methanol as the solvent permitted, as in the case of Espatite, ready separation of Na^+ from K^+.

Separation of Li^+, Na^+, and K^+ on SDV-3. The work was carried out on a column 17 cm long and containing 10 g of resin. In Fig. 4 are shown the results obtained on using 0.1 N HCl. In water (Fig. 4a) the zones of all three cations overlapped. In 60% methanol (Fig. 4b) a good quantitative separation of all the ions was effected. Again in this case, as was the case with Espatite and KU-2, potassium was not eluted with 0.1 N HCl.

On carrying out a separation in a medium of 60% acetone (Fig. 4 c) satisfactory results were obtained. The interval between Li^+ and Na^+ in the eluate was about 50 ml, while that between Na^+ and K^+ was about 100 ml. In this case, K^+, just like the other cations, was eluted with 0.13 N HCl aqueous acetone.

Attempts to accelerate separation by using 0.28 N acid were less successful (Fig. 5). Naturally, in water, all the zones overlapped. In 60% methanol the Na^+ and Li^+ zones overlapped to an insignificant extent, potassium was separated satisfactorily.

Complete separation was achieved on using 80% methanol as solvent (Fig. 6). On eluting with 0.12 N HCl, the interval between lithium and sodium was about 120 ml. In order to cut down on the time, it was found expedient after eluting the lithium with 0.1 N acid, to elute sodium with 0.2 N HCl in 80% methanol, while potassium was then eluted by using a still more concentrated aqueous solution of HCl. We used 0.12 N and 0.24 N solutions of HCl in 80% methanol, and 0.6 N aqueous HCl (Fig. 6 b). The elution rate was 5.4 ml/minute.

Accordingly, it is not possible to separate mixtures of Li^+, Na^+, and K^+ on SDV-3 in aqueous solutions. The use of aqueous organic solvents gives rise to conditions under which rapid quantitative separation of these ions becomes possible.

SUMMARY

Quantitative separation of sodium and potassium in an aqueous medium is possible on Espatite and KU-2.

In aqueous media it is not possible to separate lithium from sodium, either on Espatite or on SDV-3.

On carrying out separations on sulforesins in a medium of mixed solvents, there is a considerable improvement in separation of mixtures of lithium, sodium, and potassium.

From a practical point of view, the most suitable method is chromatographic separation on SDV-3 resin, using 0.12 N and 0.25 N solutions of HCl in 80% methanol for eluting lithium and sodium respectively, and then using a more concentrated aqueous solution of HCl for eluting the potassium.

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DETERMINATION OF SMALL AMOUNTS OF COPPER IN METALS BY MEANS OF TETRAETHYLTHIURAMDISULFIDE (DICUPRAL)

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Tetraethylthiuramidisulfide $(C_2H_5)_2NC(S) \cdot S \cdot S \cdot (S)CN(C_2H_5)_2$ has been used for the detection [1] and photometric determination of copper [2-4]. It is readily available since it is used as an accelerator for rubber vulcanization, and is also used in tablet form as an effective means of curing alcoholism, for the latter purpose it is marketed under the names "Refusal","Antabuse", "Stopetil", etc. From such tablets it is possible to prepare pure tetraethylthiuramdisulfide by recrystallization in hot ethanol. The pure material is sparingly soluble in water, it is more soluble in organic solvents, e.g., ethanol, it exists in the form of almost colorless crystals with a melting point of 70°. An alcoholic solution of tetraethylthiuramdisulfide reacts with cupric salts Cu^{2+} in weakly acid solutions to form an intensely yellow-brown colored compound; all the other elements studied do not give such colored compounds. We propose to call tetraethylthiuramdisulfide dicupral. Only mercurous salts and selenites interfere with the detection of copper, these being reduced to the elemental state (we have made use of this fact for the gravimetric determination of selenium).

The reaction sensitivity is as follows: on a spot plate pD = 5.70, in a micro test tube pD = 5.0, by extraction with ether pD = 7.18, and on filter paper pD = 6.48. Excess nitric acid and strong oxidizing agents interfere. The absorption maximum of solutions of the copper compound lies at 435 mμ; it is suitable for the photometric determination of copper (Fig. 1).

Dicupral is a more sensitive reagent than other reagents for copper, e.g., cupral (sodium diethyldithiocarbamate). The high selectivity of the reagent permits copper to be determined in the presence of many other elements.

Silver and mercuric ions form colorless compounds with dicupral, these compounds being more stable than the corresponding compounds of copper; accordingly, the intensity of the yellow-brown color of the copper compound with dicupral decreases and decolorization subsequently occurs on addition of Ag^+ or Hg^{2+}. Accordingly, if a test solution contains silver or mercury, excess reagent should be added in order to detect copper. On the other hand, we have used this phenomenon for the sensitive, selective determination of silver or mercury [5]. We have obtained very good results during the determination of mercury [6] or silver [7] in mineral raw materials, particularly in ores.

The photometric determination of copper by means of dicupral has justified itself in many instances, and is being used in various laboratories. One can point out for example the determination of not more than 0.005% of Cu in carbonates [8], or in the most diverse ores [9], in special forms of phosphates [10], in technical alkalis [9], in steel [11], in the blood plasma of children suffering from chest diseases (using 0.3 ml of sample) [12], etc.

The nature and the concentration of acid in solution affect the rate at which the maximum color intensity is reached, and also affect the nature of the calibration curve. In the work described here we concentrated on the optimum conditions in various media. At the same time we studied the effect of a large excess of various metals during the photometric determination of copper, and established that in many cases it is possible to determine copper in pure metals at a level of 0.01% Cu, without preliminary separation of the copper.

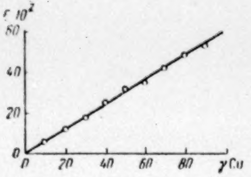

Fig. 1. Calibration curve for the determination of copper.

EXPERIMENTAL

The reagents used were as follows: a 0.01 M (0.3%) solution of tetraethylthiuramdisulfide (dicupral) in 96% ethanol. The solution of cupric sulfate (0.01 M) was prepared from the crystalline salt, the copper content was determined electrolytically. In order to maintain the hydrogen ion concentration constant, acetic (pH 4.7) and phosphoric (pH 7.0) buffer solutions were used, in addition to a dilute solution of KOH (pH 10.1); the pH was controlled by means of a glass electrode.

Twice distilled water was used for diluting the solutions. All the reagents used were checked beforehand for their copper content.

The optical density was measured on a Coleman Junior spectrophotometer type 6A with cells having a layer thickness of 16 mm, and also on a Fisher spectrophotometer AC with a blue filter 425 B, and a Pulfrich photometer.

a) Effect of the Medium. As noted already, the concentration of acid in solution affects the reaction of copper with dicupral. During a study of this reaction in media containing various acids (hydrochloric, sulfuric, nitric, and phosphoric) of differing concentrations, and also in buffered solutions (pH 4.7 and 7.0), and in weakly alkaline media, the rate at which the color intensity reached its maximum, and the stability of the color were compared. 20 μg and 50 μg of copper were taken; in both instances similar results were obtained. The procedure adopted was as follows: into a 25 ml standard flask was measured out standard solution containing exactly 20 μg or 50 μg of copper; distilled water, acid, or buffer solution was added until a definite final concentration of acid or a definite pH was reached; 6 ml of 96% alcohol was then added, followed by 3 ml of 0.01 M dicupral solution, and the solution finally made up to the mark with 96% alcohol; after mixing, the optical density was measured using a blue filter 425 B.

It is evident from the Table that with increasing acid concentration the reaction rate also increases; in strongly concentrated acid media the maximum color intensity is reached very rapidly, however, the intensity drops rapidly. In dilute acid media, and in the buffered solutions, although the reaction proceeds more slowly, the stability of the color is more than sufficient for measurement purposes.

With increasing acid concentration not only does the rate at which the color develops increase, but the color is more intense (Fig. 2).

For practical purposes it can be concluded that the calibration curves should be constructed on the basis of solutions with the same acidity as that of the test solutions. Acidity changes within small limits (1-2 N $HClO_4$, or 0.5-2N H_2SO_4, 0.5-1 N H_3PO_4, 0.1-0.5 N HCl, or 1-2 N HCl) have almost no effect on the optical density. Nitric acid at concentrations higher than 0.08 N interferes, since it reacts with the reagent. The best technique is to use a sufficient amount of the appropriate (e.g. acetic) buffer. It is necessary to carry out a careful control test for each determination, since dicupral itself acquires a weak yellow color on increasing the acidity of the solution (Fig. 3). This color is most clearly evident in hydrochloric acid solutions, since it increases directly with the concentration (even very pure hydrochloric acid usually contains traces of copper); this color does not develop in perchloric and sulfuric acids.

The presence of some organic acids (oxalic, tartaric) does not interfere with the reaction between copper and dicupral ; on the other hand, the presence of ascorbic acid, fluorides, borax, and cyanides interferes with the determination.

The absorption maximum of the colored compound of copper changes insignificantly in various media (Fig. 4).

The following useful conclusions can be drawn from the experiments we carried out: it is best to determine copper in weakly acid buffered solutions at pH 7; in more acid and strongly acid solutions the optical density should be measured within the time limits indicated in the table.

Stability of the Color of the Compound of Copper with Dicupral (20 μg Cu in 25 ml)

Medium	Time required	Time for which the color is stable
H_2SO_4, *N*		
8	10	20 min
6	10	2 hr
4	10	5 hr
2	20	5 hr *
1	20	5 hr *
0,1	30	5 hr *
0,01	30	5 hr *
HCl, *N*		
4	50	45 min.*
2	15	5 hr *
1	15	5 hr *
0,1	30	5 hr *
0,01	30	5 hr *
0,001	30	5 hr *
$HClO_4$, *N*		
4	10	30 min
2	15	2 hr
1	15	2 hr
0,1	15	5 hr
0,01	15	5 hr
H_3PO_4, *N*		
6	10	5 hr
4	10	5 hr
2	10	5 hr
1	10	5 hr
HNO_3		
0,05 *N*	15	2 hr
0,08 *N*	15	1 hr
pH 4,6	15	5 hr
pH 7,0	25	5 hr
pH 0,1	20	5 hr
5% Oxalic acid solution	10	3 hr
5% Tartaric acid	20	5 hr

*Color constant after 24 hours.

b) Determination of Traces of Copper in Metals. We have already noted previously [3] the high selectivity of the determination of copper. In those cases where, at high concentrations of certain metals, high results are obtained because these metals give a very weak color similar to the color given by copper, interference on the part of such metals can be eliminated, to a significant extent, by addition of Complexon III. But in such cases all the work should be carried out in fairly acid media in which copper does not react with Complexon III.

We checked on the possibility of determining copper in synthetic mixtures containing large amounts of zinc, aluminum, mercury, tin, arsenic, antimony, tungsten, and manganese, and demonstrated that it is possible to determine copper in pure zinc and in pure aluminum without separation.

The synthetic mixtures contained 25 μg or 50 μg of copper in 25 or 50 ml of solution. The synthetic mixture was prepared as follows: to a standard flask containing the copper solution was added a solution of the salt of the appropriate metal in gradually increasing amounts until the ratio of copper to metal was 1:10,000, and, in individual cases, 1:20,000, this corresponded to a content of 0.01 to 0.005% of copper in the metal. The acidity of the solution was adjusted to the optimum value, water was added to bring the volume to half the total volume, 6 ml of 96% ethanol was added, followed by 3 ml of 0.01 M dicupral, the volume was made up to the mark with ethanol and the whole thoroughly mixed. The optical density was measured after a certain time indicated in the table for a given acidity; a control test was carried out with pure copper and with a solution of metal not containing copper. Such an order for carrying out the reactions must be accurately observed, particularly because an unsuitable ratio of water to ethanol can lead, in certain cases, to precipitation of the salt or of the reagent.

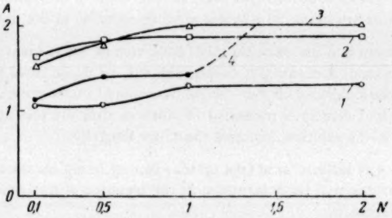

Fig. 2. Relation between the optical density of the compound of copper with dicupral and the acidity of the medium. 1) HCl, 2) H_2SO_4, 3) $HClO_4$, H_3PO_4. 40 μg Cu taken (Measurements were made after the color intensity had reached its maximum.)

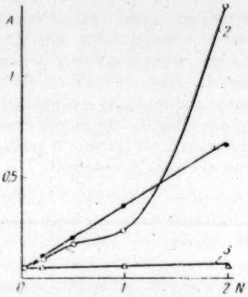

Fig. 3. Relation between optical density of dicupral and acid concentration. 1) HCl, 2) H_2SO_4, 3) H_2SO_4 and $HClO_4$.

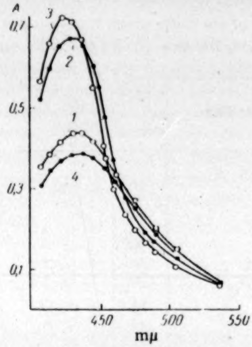

Fig. 4. Absorption of the compound of copper with dicupral in various media. 1) pH 7, 2) HCl, 3) H_3PO_4, H_2SO_4 and $HClO_4$, 4) pH 4.7.

Copper in Zinc. Measurements are carried out in a medium of 2-4 N sulfuric acid; at ratios of Cu:Zn = =1:20,000 (0.005% Cu in Zn) copper can still be determined. The optical density is measured 20 minutes after completion of the reaction.

Copper in Aluminum. Measurements are carried out in 1 N hydrochloric acid. At a ratio of 1:20,000 (0.005% Cu in Al), copper can still be determined. Optical density is measured 30 minutes after completion of the reaction. For quantities of aluminum greater than 10,000 times that of copper, it is useful to add Complexon III.

Copper in Mercury. [5] It is known that mercury ions form a more stable complex than copper with dicupral, but the complex with mercury is colorless; when large amounts of mercury are present no color develops from the copper since the reagent is used up for forming the complex with the mercury ions. Accordingly, a sufficient amount of a solution of Complexon III is added, since mercury gives an even more stable complex with Complexon than it does with dicupral. But, even in this case, copper can only be determined in mercury at a ratio of Cu:Hg of 1:2,000 (0.05% Cu in Hg). The optical density is measured in 1 N hydrogen chloride, 20 minutes after completion of the reaction.

Copper in Tungsten. For preparing synthetic samples, mixtures of solutions of cupric sulfate and sodium tungstate are used. In weakly alkaline solutions (pH 10.1) it is possible to determine copper at a ratio of Cu:W = = 1:10,000 (0.01%). Measurements are made 20 minutes after completion of the reaction.

Copper in Tin. In the presence of divalent tin salts, reduction of the reagent occurs, and the yellow color of the copper complex is decolorized; accordingly, copper can only be determined in the presence of quadrivalent tin. In a medium of 2 N hydrogen chloride, copper can be determined in the presence of tin at a ratio of Cu:Sn = = 1:500 (0.2% Cu in Sn); the optical density is measured 20 minutes after the reaction. Even traces of divalent tin (when oxidation is incomplete) in the solution decrease the color intensity.

Copper in Manganese. In 4 N sulfuric acid (the optical density being measured 15 minutes after the reaction has been carried out) copper can still be determined in the presence of manganese at a ratio of Cu:Mn = 1:6,000 without getting any high results.

Copper in Arsenic and Antimony. In 1 N hydrochloric acid, when the optical density is measured 25 minutes after carrying out the reaction, copper can be determined in the presence of arsenic at a ratio of Cu:As (Sb) = 1:1,000 (0.1% Cu in As or Sb). When higher concentrations of arsenic and antimony are present, high results are obtained.

In order to check on the practical applicability of the method, we determined copper in aluminum and zinc, using samples containing 0.01% Cu. The test zinc (5 g) was dissolved in 25 ml of concentrated sulfuric acid, while the aluminum was dissolved in 80 ml of dilute hydrochloric acid. The solution was evaporated and then cooled, the residue was dissolved in acid of the appropriate normality in a standard flask (100 ml), so that in the solution obtained the concentration of sulfuric or hydrochloric acid was 2N or N respectively. An aliquot was taken and copper then determined by the method described above.

SUMMARY

The influence of the medium, mainly the concentration and nature of the acid, on the interaction of copper salts with tetraethylthiuramdisulfide (dicupral) has been studied. The effect of a large excess of foreign cations on the photometric determination of copper has been studied and clarified. A method has been developed for the determination of small amounts of copper in pure metals.

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DETERMINATION OF SMALL AMOUNTS OF THE RARE EARTHS IN PREPARATIONS OF PRASEODYMIUM, NEODYMIUM, SAMARIUM, TERBIUM, DYSPROSIUM, HOLMIUM, ERBIUM, AND THULIUM

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Of the spectrographic methods for controlling the purity of preparations of the rare earths (r.e.), the most acceptable is analysis on the basis of their emission spectra, which permits all the rare earths to be determined without exception, and is characterized by a high, absolute sensitivity. As is evident from Table 1, Fassel and coworkers [2-4] have been mainly responsible for work on the determination of impurities in purified preparations of the rare earths on the basis of their emission spectra. According to the technique they have developed, an aliquot of 15 mg, which is a mixture of the rare earth oxides in the form of a powder, is completely burnt in a d.c. arc (17-18 amps, 220 volts) between carbon electrodes.

During the analysis of rare earth preparations using a Russian diffraction spectrograph, the DFS-3, with a dispersion of 2 A/mm in the first order, the standards and samples for quantitative determination of the impurities in the rare earths are usually prepared in the form of 5% (in terms of the metal) solutions of the rare earth chlorides in 1% HCl [10]. A drop of the solution is placed on the flat end of a copper or carbon electrode which had been covered beforehand with a film of polystyrene. After drying off the drop, there remains on the electrode face a fine layer of test material. The spectrum is excited in an a.c. arc (8 amps, 220 volts). As was shown in [10], the use of the DFS-3 spectrograph for emission analysis of purified preparations of the rare earths, despite the complexity of their spectra, made it possible to determine hundredths of a percent of the impurities which are neighbors of the rare earth series of elements. For this purpose not more than 1 mg of test material is necessary.

TABLE 1

Base	Gatterer, Jumhkes, [1]	Fassel et al. [2-4]	Shvangiradze [5, 6]	Akimov [7]	Polyakov Rusanov [8]	Brukl, Rossmanith [9]	Our results
			Impurities determined				
La	—	Ce, Pr, Nd	Ce, Pr, Nd	Ce, Pr	Ce, Pr, Nd	—	—
Ce	—	La, Pr, Nd	La, Pr	—	La	—	—
Pr	—	La, Ce, Nd	—	—	—	—	La, Nd
Nd	—	Pr, Sm	Pr, Sm	—	—	—	Pr, Sm
Sm	Eu	Eu	Eu, Nd	Nd	—	Eu, Nd	Eu, Nd
Eu	—	—	—	—	—	Sm	—
Gd	—	—	—	—	—	—	—
Tb	—	—	—	—	—	—	Gd, Y
Dy	—	Y, Tb, Ho, Er	—	—	—	—	Y, Ho
Ho	—	Y, Dy, Er	—	—	—	—	Dy, Er
Er	—	Y, Dy, Ho, Tu, Yb	—	—	—	—	Ho, Tu
Tu	—	—	—	—	—	—	Er, Yb

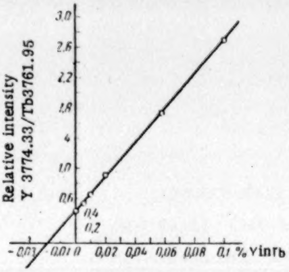

Fig. 1. Relation between the relative intensity Y 3774.33 / Tb3761.95 and the yttrium concentration of the standards.

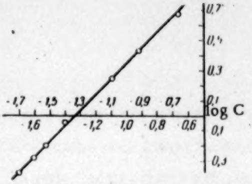

Fig. 2. Calibration curve for the determination of yttrium in terbium by means of the lines Y 3774.33 / Tb 3761.95.

In the work described here small amounts of the impurities shown in Table 1 were determined in purified preparations of terbium, dysprosium, thulium, and samarium by the technique described previously [10]. In addition, the method for the determination of impurities in erbium, holmium, and praseodymium was made more accurate.

In view of the lack of information, for our purposes, regarding the emission spectra of the rare earths, the choice of the most sensitive lines of the impurities, which were free from superposition by other lines, was made as follows. The spectra of a series of preparations, obtained, for example, during the purification of terbium preparations from yttrium and gadolinium by the method of ion exchange chromatography, were studied in the region between 3000 and 4600 A. For the determination of yttrium in terbium preparations, those lines were chosen which were most intense in the spectrum of the terbium preparation strongly contamined with yttrium and not detected in the spectrum of a terbium preparation containing the highest amount of gadolinium. The reference lines chosen were those lines lying nearest to the analytical lines of the impurity, and which belong to the element forming the major component of the test sample, and for which the value log R (R is the relative intensity) exhibits the least shift on photographing the spectrum of the same standard 5-6 times on one plate, or taking two photographs on 2-4 plates.

TABLE 2

Determination of	Analytical lines	Range of concentrations determined, %	Electrodes
Y in Tb	Y 3774,33/Tb 3761,95	0,02 —0,2	Copper
Gd in Tb	Gd 3768,41/Tb 3761,95	0,02 —1	The same
Y in Dy	Y 3774,33 Dy 3777,99	0,007—0,2	" "
Dy in Ho	Dy 4211,72 Ho 4219,13	0,02 —1	" "
Ho in Er	Ho 4103,84/Er 4104,01	0,02 —1	" "
Tu in Er*	Tu 3362,61/Er 3369,22	0,005—1	Carbon
Yb in Tu**	Yb 3289,37/Tu 3291,00	0,05 —1	The same
Yb in Tu	Yb 3987,99/Tu 3926,74	0,005—0,2	Copper
Er in Tu	Er 3906,32/Tu 3912,90	0,02 —1	The same
La in Pr	La 3337,49/Pr 3340,53	0,005—0,1	Carbon
Nd in Pr	Nd 43 8,17/Pr 4356,67	0,1 —1	The same
Sm in Nd***	Sm 4433,87/Nd 4436,68	0,05 —1	" "
Pr in Nd***	Pr 4408,84/Nd 4419,62	0,1 —1	" "
Nd in Sm	Nd 4303,57/Sm 4300,16	0,02 —1	" "
Eu in Sm	Eu 3819,66/Sm 3818,35	0,005—0,2	Copper

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*When the concentration of impurities is > 0.1%, 1% solutions can be used.

**For determination of Yb in Tu in the given concentration range, we used a 0.05% solution of Tu in 1% HCl.

***These pairs of lines are given in [3].

TABLE 3

Determination of:	Initial content of impurity, %	Added, %	Total	Found, %	Error, %
Y in Tb	0,02	0,02	0,04	0 042	5
	0,02	0,02	0,04	0,038	5
Gd in Tb	0,04	0,1	0,14	0,146	4,3
	0,04	0,1	0,14	0,135	3,5

Calibration curves of log R against log c (c is the concentration in % of the impurity in the standard) were constructed for the chosen analytical pairs of lines.

For preparing the standards, the most pure preparations of the rare earths obtained during separation by ion exchange chromatography were used. Sensitive lines for yttrium were detected in the spectra of the purest terbium and dysprosium preparations, while in the spectrum of a samarium preparation the last lines of europium were found. The concentration of these impurities was determined by the method of additions [11]. In Fig. 1 are given the calibration curves*, within the coordinates R, c, which illustrate the determination of the residual yttrium as an impurity in the purest sample of terbium, on the basis of which standards of Tb and Y were prepared. As is shown in Fig. 1, the yttrium content is 0.019%. After applying this correction for the yttrium content in the standards, the calibration curve of log R against log c in the concentration range 0.02 to 0.22% was linear, and was used for the determination of yttrium present as an impurity in more impure samples. (Fig. 2). 0.007% of yttrium was found in the dysprosium preparation, while the amount of europium in a samarium preparation was 0.004%.

Table 2 contains the analytical lines which we chose, the concentration ranges for which the curves used for determining the impurities were linear, and the electrodes used.

The conditions used for taking the spectra of the rare earths being determined are given in a previous article [10].

Curves during the construction of which the residual impurities were taken into account, and were based on standards whose spectra had been photographed on 2-6 plates, preserve a constant slope (about 45°) and do not exhibit any shift. The mean arithmetic error during determination of the concentration (calculated from four experimental results) amounts to about 5%.

In order to check on the correctness of the determination of the impurities by the method indicated [10], control standards were prepared. Into a preparation containing the impurity element in an amount established beforehand, was added a known amount of the same element, after which the total amount of the element was determined. Table 3 contains as examples some of the results obtained during such determinations.

The author would like to thank G. K. Eremina and L. I. Martynenko for gifts of rare earth preparations, and V. N. Tatevskii and L. V. Lipis for helping in the work.

SUMMARY

As a result of a study of the spectra of lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, terbium, yttrium, dysprosium, holmium, erbium, thulium, and ytterbium, in the region 3000 to 4600 A, analytical lines have been chosen which are suitable for determining hundredths of a percent of the rare earths listed.

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*The graphical method for calculating the concentration of residual impurity in the test preparations [11] holds for the conditions $R = ac^V$, $v = 1$. As is evident from Fig. 1. this is the case for the determination of yttrium in terbium.

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THE PHOTOMETRIC DETERMINATION OF TITANIUM IN TITANIUM BORIDES BY MEANS OF ARSENAZO

E. I. Nikitina

Arsenazo, or benzene-2-arsonic acid < 1-azo-2 > 1, 8-dihydroxy-naphthalene-3, 6-disulfonic acid, is used for the photometric determination of the rare earths [1], zirconium [2], aluminum [3], and tantalum [4]. Arsenazo in aqueous, neutral and acid solutions, has a rose color: in the presence of titanium the color changes to violet at a pH of 2-3. On increasing the acidity, the color of the compound of titanium with arsenazo gradually weakens, and at a pH of 0.7-0.8, disappears completely [4]. The relation between the color of the complex of titanium with arsenazo and the pH of the solution is shown in Fig. 1.

In solution at pH 2.5-3, titanium forms a more stable colored complex compound with arsenazo: the optical density of the solution in this acidity range remains almost constant for 0.01-0.25 mg of titanium. The solution conforms to the Beer law for amounts of 0.01 to 0.25 mg of titanium (Fig. 2). The color of the titanium complex with arsenazo is readily reproducible and is fully suitable for the photometric determination of titanium. The colored, soluble compound of titanium with arsenazo is formed at room temperature immediately after addition of reagent to a weakly acid solution of a titanium salt. The color intensity does not change on heating the solution. The color of the titanium-arsenazo compound is stable for several days. The reaction of titanium with arsenazo is considerably more sensitive than the reaction with hydrogen peroxide. It permits determination of 0.05 γ of titanium in one ml. The nature of the mineral acid does not affect the colored compound of titanium with arsenazo—it develops at pH 2-3 in hydrochloric and sulfuric acid solutions.

Titanium is best determined photometrically with arsenazo on the basis of the mixed color obtained from excess reagent and the violet color of the titanium complex. The mixed color is obtained on adding 10 ml of a 0.05% solution of reagent, for titanium contents ranging from 0.01 to 0.25 mg of titanium in 100 ml of solution.

The maximum light absorption of the titanium complex at pH 2.5-3 is located at 580 mμ (Fig. 3). In this spectral region the solution of pure arsenazo has minimum light absorption.

The results given in Table 1 show the good reproducibility obtained during the determination of titanium with arsenazo. The reagent is so sensitive to titanium, and the color is so intense, that in order to measure 0.25 mg of titanium, a cell with a layer thickness of 20 mm should be used. The zero solution used consists of 10 ml of arsenazo solution and 90 ml of water.

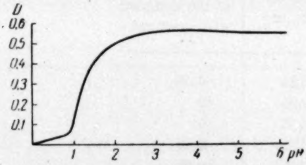

Fig. 1. The relation between the color of the titanium complex with arsenazo and the pH of the solution.

In the presence of oxalates and fluorides the compound of titanium with arsenazo is not formed (Table 2). Tartaric or citric acid in a sulfuric acid solution slightly depresses the intensity of the color of the titanium arsenazo complex (Table 2), but the sensitivity of the reaction remains unchanged (0.05 γ titanium in 1 ml).

The alkali and alkaline earth metals do not interfere with the determination of titanium by means of arsenazo. Ferric iron (up to 0.03 mg), and trivalent chromium (< 0.1 mg) present in the solution being analyzed do not interfere either with titanium determination.

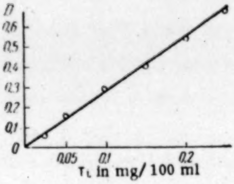

Fig. 2. Relation between the color of the titanium complex with arsenazo and the titanium concentration of the solution at pH 2.5-3.

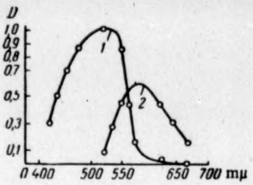

Fig. 3. Light absorption curves of the complex of titanium and arsenazo: 1) Reagent 2) titanium complex.

TABLE 1

Determination of Titanium with Arsenazo (in mg)

Ti taken, mg	Ti found, mg	
0.01	0.01	0.012
0.06	0.06	0.058
0.10	0.10	0.105
0.12	0.12	0.13
0.16	0.17	0.155
0.20	0.21	0.21
0.25	0.25	0.24

The photometric method of determining titanium with arsenazo has been successfully used for determination of large amounts of titanium in titanium metal and in two samples of titanium and chromium boride (Table 3).

Analytical Procedure. 0.2 g of titanium boride, titanium metal, or the double boride of titanium and chromium is dissolved in 20 ml of sulfuric acid (1:1) containing 7 ml of hydrogen peroxide. The latter is added until the titanium boride has dissolved completely. The solution is heated until white fumes are evolved; during this stage the solution is decolorized and the hydrogen peroxide is decomposed. The solution is poured into a 100 ml standard flask. When an insoluble residue remains, this is filtered off, washed, and then fused with potassium pyrosulfate, the solution of the melt obtained is combined with the main solution and the volume made up to the mark with water. 5 ml of this solution is measured out into a 200 ml standard flask in which it is diluted to the mark with water and thoroughly mixed. By this means the requisite pH is obtained. 5 ml of this solution in the

TABLE 2

Effect of Masking Agents

Masking agent	Concentration g/ml	Titanium taken, mg	Optical density of the complex with arsenazo
–	–	0.125	0.38
Hydrofluoric acid	0.0002	0.125	0
Oxalic "	0.025	0.125	0
Tartaric "	0.125	0.125	0.34
Citric "	0.0125	0.125	0.36

TABLE 3

Determination of Titanium in Borides and Titanium (sample weight 0.2 g)

Test material	Titanium, %		Iron content %
	amount present*	amount found	
Titanium metal	97,0	97,2	3,0
	97,0	97,2	3,0
	97,0	96,5	3,0
	97,0	96,5	3,0
	97,0	97,4	3,0
Titanium boride	66,6	66,9	2,0
	66,6	66,5	2,0
	66,6	66,9	2,0
	66,6	66,6	2,0
	57,10	57,3	1,5
	57,10	57,5	1,5

*Determined by the cupferron method.

200 ml flask is measured out into a 100 ml flask and 10 ml of arsenazo solution added, the volume is made up to the mark with water and the whole mixed; the optical density is measured in a cuvette with a layer thickness of 20 mm, an orange filter being used (6-FÉK-N). The amount of titanium in titanium boride is found by comparing the optical density of the solution obtained with the optical density of a solution of titanium metal containing a known amount of titanium, and prepared under similar conditions. The accuracy of the method is ± 0.4%.

SUMMARY

A quantitative method has been developed for the photometric determination of titanium with arsenazo; the latter forms with titanium a stable, soluble, violet colored compound at pH 2.5-3. The method permits the determination of 0.01 mg and more of titanium.

The method has been used for the determination of large amounts of titanium (up to 70%) in titanium boride.

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AN EXTRACTION PHOTOMETRIC METHOD FOR THE DETERMINATION OF THORIUM IN NATURAL MATERIALS

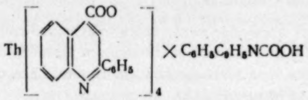
L. I. Gerkhardt

The reagent arsenazo which was suggested by V. I. Kuznetsov [1] for the determination of thorium and uranium, is widely used in various analytical methods [2, 3].

The basis of the method described here is the precipitation of thorium with phenylcinchonic acid (atophan), followed by its extraction as the phenylcinchonate with n-butanol from weakly acid solutions (pH 2.5-4.5), and its final determination with arsenazo in an aqueous-organic medium (acetone-butanol-water) in the presence of tartaric * and citric acids [4].

Precipitation of thorium at pH 2.5-4.5 was carried out with a tenfold excess of 2% aqueous solution of ammonium phenylcinchonate, the latter was prepared as follows [7]. 2 g of phenylcinchonic acid was treated with 10% ammonia solution in a porcelain basin, and heated on a water bath until the odor of ammonia had dissappeared. The dry residue was dissolved in 100 ml of water or butanol.

The chemical composition of thorium phenylcinchonate was established on the basis of the difference between the amount of phenylcinchonic acid which reacts with the thorium ions, and the free acid found by titration with 0.1 N sodium hydroxide in the presence of phenolphthalein [7]. The results obtained show that the composition of thorium phenylcinchonate corresponds to the formula:



The extractability of thorium phenylcinchonate with amyl acetate, n-butanol, isoamyl alcohol, acetylacetone, methyl butyl ketone, and chloroform was studied (Table 1).

It is evident from Table 1 that butanol and amyl acetate extract thorium quantitatively; butanol was used as the extracting agent.

Extraction of thorium phenylcinchonate with butanol is possible in the pH range 2.5-4.5 (Fig. 1). The pH of the test solutions was established by means of 0.09 N hydrochloric acid and 1 M ammonium acetate solution. Into the solution containing thorium ions (Table 2) was added 2 ml of 1 M ammonium acetate solution and 0.09 N hydrochloric acid up to 10 ml; the pH of such a solution was 3-4. Thorium was then extracted with an equal volume of a 1% solution of ammonium phenylcinchonate in butanol. To the extract, after its removal from the aqueous phase, was added 5 ml of acetone, and 3 ml of 0.05% arsenazo solution in 0.09 N hydrochloric acid, and the volume made up to 25 ml with 0.09 N acid; the whole was mixed and the optical density measured in 30 ml cuvettes on a FÉK-M photocolorimeter using a yellow-green filter (570 mμ), relative to a zero solution containing the same reagents.

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* Determination of thorium with thoron in the presence of tartaric acid has been described in [6].

TABLE 1

Distribution of Thorium between the Organic and Aqueous Phases in %

Extracting agent	Distribution		Partition coefficient
	extracting agent	water	
Amyl acetate	100	0,00	—
Butanol	100	0,00	—
Isoamyl alcohol	91,76	8,24	11,13
Acetylacetone	80,08	19,92	4,02
Methyl butyl ketone	31,51	68,49	0,46
Chloroform	6,21	93,79	0,07

The amount of thorium was determined by means of a calibration curve which was constructed in similar fashion, using solutions containing 10, 15, 20, and 70 γ of thorium in 25 ml of the aqueous organic solution.

Thorium is quantitatively extracted from hydrochloric acid solutions at a pH of 2.5-4.5 by means of butanol (Table 2).

Solutions of the complex of thorium with arsenazo in the aqueous organic medium are more stable than solutions of this complex in water [2, 3, 5]; the optical density of such solutions remains unchanged for several days. The maximum light absorption of the aqueous organic solutions of the thorium arsenazo complex is located at 570-575 mμ (Fig. 2) just as that of the aqueous solutions. The molar extinction coefficient of the thorium arsenazo complex, as found by the saturation method [8, 9] at several wavelengths, is equal to 29000 at 570 mμ.

In order to study the relation between the optical density of the thorium arsenazo complex and the pH of the solution in an aqueous organic medium, 3 ml of 0.05% arsenazo solution and the appropriate amount of 1 M ammonium acetate were added to 1 ml of thorium solution (28 γ Th). The pH was controlled potentiometrically. The optical density was measured on a FĚK-M photocolorimeter at 570 mμ.

From Fig. 3 it is clear that on increasing the pH from 0.5 to 1.5, the optical density also increases; afterwards, up to pH 2.5, the optical density remains constant. Complete complexing of the thorium occurs at pH 1.5, this indicates the high stability of the complex.

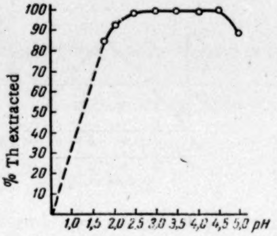
The relation between the light absorption of the thorium arsenazo complex and hydrogen ion concentration was determined. The optical density of a solution of the thorium arsenazo complex was measured on a SF-4 spectrophotometer at various wavelengths, at a layer thickness of 10 mm. The maximum light absorption, starting at pH 1.5 right up to 2.5, was found at 570 mμ (Fig. 4).

The effect of the amount of arsenazo on the optical density of the thorium arsenazo complex in an aqueous organic medium was studied. On measuring the optical density of the complex in comparison with a solution of

TABLE 2

Determination of Thorium in Pure Solutions, γ

Taken	Found	Error
4.83	4.5	-0.33
19.34	19.5	+0.16
18.0	18.0	0.00
28.6	28.5	-0.10



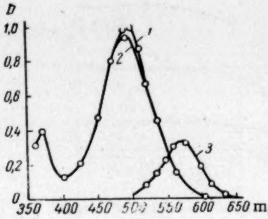


Fig. 1. Effect of pH on the extraction of thorium by n-butanol.

Fig. 2. Light absorption of solutions of arsenazo I and of the complex of thorium with arsenazo (concentration 2.9 x 10^{-5} M, SF-4 cuvette 10 mm). 1) Arsenazo in an aqueous organic medium; 2) the thorium arsenazo complex in an aqueous organic medium; 3) the thorium arsenazo complex plus arsenazo in an aqueous organic medium.

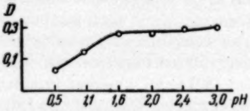


Fig. 3. Effect of pH on the optical density of the thorium arsenazo complex (570 mμ).

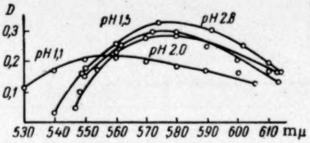


Fig. 4. Light absorption of the thorium arsenazo complex as a function of the ph of the medium.

the reagent in an aqueous organic medium at 570 mμ and at a pH of 1.5-2.0, it was established that the highest optical density is found in the presence of two milliliters of 0.05% arsenazo solution (Fig. 5). A further increase in the amount of the arsenazo solution did not alter the optical density of the solution.

The composition of the thorium complex with arsenazo in an aqueous organic medium was established by the isomolar series method [10, 11]. The maximum on the curve composition–optical density corresponds to a molar ratio of thorium to arsenazo of 1:1 (Fig. 6). These results were also confirmed by the method of the ratio of the slopes of the curve [12] (Fig. 7). For this purpose two series of solutions were prepared, one of which had differing concentrations of thorium in the presence of a constant excess of reagent, while the other had a constant concentration of thorium for variable concentrations of reagent, expressed in moles per liter. The optical density was measured at 570 mμ. The results given in Fig. 7 confirm that the ratio of thorium to arsenazo in the complex is 1:1.

In order to determine thorium in the presence of titanium and zirconium, ascorbic acid (1-2 mg) was added to the test solution, followed by 2 ml of 1 M ammonium acetate solution, and the volume made up to 10 ml with 0.09 N hydrochloric acid; this solution was extracted with an equal volume of a 1% solution of ammonium phenylcinchonate in butanol. After removing the extract from the aqueous phase, it was dissolved in 5 ml of acetone, 3 ml of a 0.05% arsenazo solution prepared in 0.09 N hydrochloric acid was added, this was followed by 0.5 ml of 10% tartaric acid, and 3-5 mg of ascorbic acid, and the optical density measured as described above.

Ascorbic acid in this medium forms with titanium a complex compound which is not extracted by butanol. Zirconium and titanium (Table 3) are not quantitatively extracted with butanol in the presence of ascorbic acid. During extraction of thorium as its phenylcinchonate by means of butanol, traces of titanium and zirconium pass into the extract, but interference on their part is prevented by addition of tartaric and ascorbic acid.

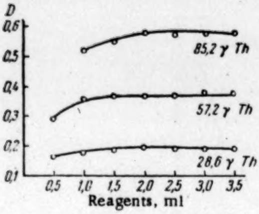


Fig. 5. Effect of the amount of reagent on the optical density of the thorium arsenazo complex.

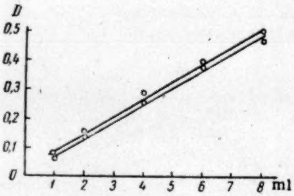


Fig. 7. Determination of the composition of the thorium arsenazo complex by the method of the ratios of the slopes of the curves.

TABLE 3

Distribution of Zirconium and Titanium in the Presence of Ascorbic Acid

Amt.in mg/10 ml		Distribution, mg			
		Zr		Ti	
Zr	Ti	butanol	water	butanol	water
1,0	—	0,40	0,60	—	—
1,0	—	0,40	0,60	—	—
1,0	—	0,30	0,70	—	—
1,0*	—	1,00	0,00	—	—
—	1,0	—	—	0,05	0,95
—	1,0	—	—	0,10	0,90
—	1,0	—	—	0,03	0,97
—	1,0*	—	—	0,90	0,10

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*Ascorbic acid not added.

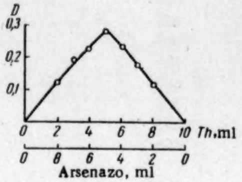

Fig. 6. Determination of the composition of the thorium arsenazo complex by the isomolar series method.

It is clear from Table 4 that thorium can be determined in the presence of titanium and zirconium by the given method with a permissible error.

The effect of iron and uranium during the extraction-photometric determination of thorium was studied under the same conditions. Ascorbic acid reduces iron (III) to the divalent state which does not interact with phenylcinchonic acid; uranium (VI) gives a colores complex compound with ascorbic acid [13], and, just like titanium, is not extracted with butanol. In addition, uranium (VI) forms a colored complex with arsenazo in neutral media. In acid media (pH < 4) uranium does not interfere.

The results given in Table 5 indicate that it is possible to determine thorium in the presence of iron.

Ions of uni- and divalent metals (Na^+, Ca^{2+}, etc.) do not interact with phenylcinchonic acid, and are not extracted with butanol; trivalent elements, including the rare earth element [14], vanadium, molybdenum, and tungsten, in the presence of ascorbic acid, do not give phenylcinchonates either, and are not extracted with butanol.

It is clear from Table 7 that I, II, and III group elements, and also vanadium, molybdenum, and tungsten do not affect thorium determination.

A Method for Determining Thorium in Ores and Minerals

Five to fifty mg of ore or mineral was fused in a porcelain crucible with 1.5-2 g of sodium peroxide, in a muffle at 550°, until a homogeneous melt was obtained. The cooled melt was dissolved in 30 ml of water; after heating for 10-15 minutes the precipitate was filtered off, washed 2-3 times with cold water, and then dissolved on the filter paper in 5-10 ml of 5% (by volume) of hot hydrochloric acid; the solution was neutralized with ammonia to a pH of 2.5-3.0 (congo red paper); the solution was then transferred into a 25 ml standard flask, in which its volume was made up to the mark with 0.09 N hydrochloric acid.

TABLE 4

Determination of Thorium in the Presence of Titanium and Zirconium

Amount taken in 10 ml			Th found, γ	Error in determining Th, γ
Ti, mg	Zr, mg	Th, γ		
0.5	0.5	4.8	4.5	-0.3
1.0	1.0	18.0	18.5	+0.5
1.0	1.0	18.0	18.5	+0.5
1.0	1.0	18.0	19.5	+1.5
1.0	1.0	18.0	17.0	-1.0

TABLE 5

Determination of Thorium in the Presence of Iron

Amount taken in 10 ml		Th found, γ	Error in determining Th, γ
Th, γ	Fe, mg		
14.0	20.0	12.5	-1.5
21.8	40.0	22.5	+0.7
21.8	100.0	20.5	-1.3
21.8	120.0	23.0	+1.2
14.0	140.0	12.5	-1.5

TABLE 6

Determination of Thorium in the Presence of Uranium (2.18 γ Th and 1 mg U in 10 ml taken)

Th found, γ	Error in Th, γ	Th found, γ	Error in Th, γ
23.75	+1.95	21.25	-0.55
21.25	-0.55	23.75	+1.95
21.25	-0.55	21.25	-0.55

An aliquot of this solution (2-10 ml) was transferred into a 20-50 ml separatory funnel, 1-2 mg of ascorbic acid and 2 ml of 1 M ammonium acetate were added and the volume made up to 10 ml with 0.09 N hydrochloric acid. The solution was thoroughly mixed, and 5 ml of a 2% solution of ammonium phenylcinchonate in butanol added, this was followed by 5 ml of butanol and the thorium than extracted for 20-40 seconds. After the layers had separated, the extract was transferred to a 25 ml standard flask and the funnel rinsed out with 5-10 ml of acetone which was mixed with the extract, 3 ml of a 0.05% arsenazo solution was then added, followed by 1-5mg of ascorbic acid, and 0.5 ml of 10% tartaric acid, the volume was finally made up to the mark with 0.09 N

TABLE 7

Determination of Thorium in the Presence of Various Ions (28.6 γ of Th taken)

Metal ions, mg/10 ml	Th found in the extract, γ	Error in Th, γ	Metal ions, mg/10 ml	Th found in the extract, γ	Error in Th, γ
Na^+ 5,0	28,8	+0,2	Zn^{2+} 5,0	29,0	+0,4
Ag^+ 5,0	28,3	−0,3	Fe^{2+} 3,0	27,5	−1,1
Cu^{2+} 3,0	29,0	+0,4	Al^{3+} 5,0	28,3	−0,3
Mg^{2+} 3,0	28,5	−0,1	La^{3+} 1,3	28,5	−0,1
Ca^{2+} 3,0	27,5	−1,1	Total 2,0	29,0	+0,4
Mn^{2+} 4,0	28,0	−0,6	VO_3^- 4,0	28,8	+0,2
Ba^{2+} 3,0	28,3	−0,3	MoO_4^{2-} 3,0	28,2	−0,4
Ni^{2+} 1,5	29,0	+0,4	WO_4^{2-} 3,0	28,6	0,0

TABLE 8

Determination of Thorium in Ores and Minerals, %

Main components		Found		Error (relative)
		by the given method	by method [15]	
ZrO_2 TiO_2 Fe_2O_3 Al_2O_3	6,21 6,60 55,67 12,0	0,13; 0,113	0,12	+0,8
V_2O_5 ZrO_2 Total	0,24 8,28 2,10	0,172; 0,15	0,16	+0,6
ZrO_2 Total	7,32 2,27	0,19	0,19	0,00
ZrO_2 Total	9,90 0,97	0,133; 0,141	0,14	−2,1
R_2O_3 ZrO_2 TiO_2	31,9 6,0 1,68	0,17; 0,18	0,17	+3,0
	Zircon	0,005	0,059	−15,0
	Pyrochlor	1,67	1,66	+ 0,6
	Ore	0,005	0,006	−16,0

hydrochloric acid. After 1-2 hours the optical density was measured on a FÉK-M photocolorimeter in 30 mm cuvettes at 670 mμ (with a yellow-green filter). When such a filter is not available it is necessary to combine a green filter with a liquid filter. A saturated solution of potassium dichromate can be used as the liquid filter, the dichromate being placed in a 10mm cuvette in the path of the light rays.

The amount of thorium was determined on the basis of a calibration curve which was constructed as follows: 0−5−10−15−70 γ of thorium was extracted with ammonium phenylcinchonate in butanol. The extracts were transferred into 25 ml standard flasks, 5 ml of acetone, 3 ml of 0.05% arsenazo, 1-5 mg of ascorbic acid, and 50 mg of tartaric acid were added to each flask and the volume made up to the mark with 0.09 N hydrochloric acid. The optical density was measured under the same conditions.

SUMMARY

A study has been made of the conditions for separating thorium from accompanying elements by extracting thorium phenylcinchonate with n-butanol at a pH of 2.5-4.5 in the presence of ascorbic acid.

It has been established that it is possible to determine thorium photometrically on the basis of its complex with arsenazo in the presence of tartaric and ascorbic acids in a medium of acetone–butanol–water.

An extraction-photometric method has been developed for the determination of thorium in ores and minerals by means of arsenazo I; this method permits determination of 0.005% to whole parts of a percent of thorium on small aliquots of sample, with a relative error of 5-20%.

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COMPLEXONOMETRIC AND PHOTOMETRIC DETERMINATION OF THORIUM IN MINERALS AND ORES

F. V. Zaikovskii

Large amounts of thorium (> 1-2%) are determined in monazite and other minerals and ores mainly by the iodate titrimetric method [1], or by gravimetric methods using fluoride, oxalate, and certain other anions as precipitants [2]. These methods require large aliquots of test material, repeated precipitations of the precipitates, and a determination takes 3-4 working days. Methods were published recently for the complexonometric determination of thorium using metalloindicators: pyrocatechin violet [3], alizarin [4, 5], chromazurol [6], cacothelin with Fe^{2+} [7], 2, 7-dinitroso-1, 8-dihydroxynaphthalene-3, 6-disulfonic acid [8], eriochrome cyanine [9], 1-(2-pyridylazo)2-naphthol [10] and some others.

The practical value of these indicators is not very high, particularly when applied for the analysis of mineral raw materials. The color change of the indicator at the endpoint is only clearly manifested during titration of thorium in pure solutions.

The aim of the work described here was to develop a rapid and convenient complexonometric method for the determination of large amounts of thorium, and the use of arsenazo [13] and a photometric method for the determination of small amounts of thorium in minerals and ores [11, 12].

First, a study was made of the conditions necessary for the complexonometric titration of thorium in solutions containing calcium and also titanium, zirconium, and the rare earths, using ferric thiocyanate as the indicator.

Thorium was titrated in the presence of calcium by the following method. To 20-25 ml of a hydrochloric acid solution containing thorium and calcium in the amounts indicated in Table 1, at a pH of 2-3, (congo red paper) was added 1 ml of a 30% solution of potassium (ammonium) thiocyanate, and 3-4 drops of ferric chloride solution, containing 0.1 mg of iron per ml; the final solution was heated to 60° and slowly titrated with 0.002 M Complexon III (EDTA) solution until the color disappeared on addition of one drop of solution.

Into another flask containing 20 ml of water was introduced 1 ml of thiocyanate solution, 2 drops of hydrochloric acid 1:1, and 3-4 drops of ferric chloride solution. This solution was also titrated until the color disappeared. From the number of mls of 0.002 M Complexon III solution used for titrating thorium and iron, the number of ml of this solution used for titrating iron was subtracted. One ml of Complexon III solution corresponded to 0.464 mg of thorium.

It is clear from Table 1 that calcium does not interfere with the complexonometric titration of thorium.

It is evident from Table 2 that zirconium and titanium, just like thorium, are titrated by Complexon III. During titration of thorium with Complexon III in the presence of ferric thiocyanate as indicator, a sharp change is observed at the end point (conversion of iron into the complexonate). The rare earths form stable compounds with Complexon III in a weakly alkaline medium. It is clear from Table 3 that the rare earths do not interfere with the titration of thorium.

In order to remove thorium from accompanying elements, the iodate-tartrate [11], and the acetonedioxalate method [12] were used. Thorium was separated from the greater part of the zirconium and titanium by the iodate-tartrate method; subsequently, in addition, for the quantitative removal of thorium from titanium and zirconium, thorium was precipitated with acetonedioxalic acid.

TABLE 1

Determination of Thorium in the Presence of 50 mg Calcium

Th taken, mg	0.002 M Complexon III solution used, ml	Th found, mg	Absolute error, mg
3.953	8.50	3.944	-0.009
3.953	8.30	3.851	-0.102
3.953	8.40	3.898	-0.055
1.977	4.00	1.856	-0.021
1.977	4.30	1.995	+ 0.018

Decomposition of Test Material and Preparation of the Solution for Precipitation of the Thorium. 5.00-50.00 mg of test material was placed in a 10 ml porcelain crucible containing about 1 g of sodium peroxide and 4-5 mg of ferric oxide; 1-2 g of sodium peroxide was added and the mass fused in a muffle at 550° until a homogeneous melt was obtained (2-3 minutes). The cooled melt was treated with 50-80 ml of water at 100° for 10 minutes; after 25 minutes, the solution was filtered through a 7 cm diameter "white band" filter paper, and washed 2-3 times with a 0.5% solution of sodium hydroxide. The metal hydroxides were dissolved on the filter in 9 ml of hot nitric acid 1:2, and 10 ml of hot water. The filter was washed with 5-6 ml of hot water. 1 drop of hydrogen peroxide was added and the solution cooled to 1-5°, thorium was then precipitated with iodate in the presence of tartaric acid and hydrogen peroxide.

Iodate Precipitation. To the solution was added 5 ml of a 60% solution of tartaric acid, 0.5 ml of a 3% solution of mercury nitrate, and 10 ml of a 6% solution of potassium iodate, the volume was made up to 50 ml with water and the whole thoroughly mixed. When the test material contained an appreciable amount of thorium, zirconium, and titanium a large precipitate of the metal iodates was formed. When only small amounts of these elements were present the solution merely became turbid.

At this stage of the procedure 50 ml of the solution should contain 3 ml of concentrated nitric acid (63-64%), 15 mg of mercury (II) in terms of the oxide, 3 g of tartaric acid, and 0.6 g of potassium iodate. The solution was left in a cool place for 45 minutes, after which the precipitate was filtered through a double "white band" filter paper 7 cm in diameter, using a filter aid (macerated filter paper). The filter was washed with 20-25 ml of a potassium iodate wash solution*. The precipitate on the filter was dissolved in 10-15 ml of 20% by volume, hot hydrochloric acid. The filter was washed 2-3 times with 10-15 ml of hot water. The filtrate was collected in the same beaker as that used for precipitating the thorium and then evaporated to a volume of one ml.

When the material contained large amounts of thorium, zirconium, and titanium, the oxalate precipitation was used (see below) in order to remove the thorium completely from zirconium and titanium: when only small amounts of thorium, zirconium, and titanium were present there was no need to resort to the oxalate precipitation. In the latter case, 5-6 ml of concentrated hydrochloric acid, and 5-6 drops formaldehyde solution were added the solution was then evaporated to a volume of 0.5 ml. This operation was repeated until the iodine had been removed. 6-8 ml of water was added and the pH adjusted to pH 2-3 with ammonia (congo red paper). 1% ascorbic acid solution was added until the solution was decolorized, 0.2 ml of the ascorbic solution was then added in excess. The solution was filtered into a 25 ml standard flask and the volume made up to the mark with 0.09 N hydrochloric acid, the solution was thoroughly mixed and the thorium determined photometrically [12].

Oxalate Precipitation. To the residue obtained after evaporating off the hydrochloric acid, 30-40 ml of water was added, followed by 0.5 ml of a 25% solution of calcium chloride, and sodium acetate solution dropwise

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*500 ml of this solution contained 6 g of potassium iodate, 3 ml of hydrogen peroxide, and 30 ml of concentrated nitric acid.

TABLE 2

Determination of Thorium in the Presence of Zirconium and Titanium

Th taken, mg			0.002 M Complexon III solution used, ml	Th found, mg	Absolute error, mg
Th	Zr	Ti			
3,953	0,010	—	8,53	3,959	+0,006
3,953	0,030	—	8,62	4,000	+0,047
3,953	0,060	—	8,69	4,032	+0,079
3,953	—	0,010	8,54	3,967	+0,014
3,953	—	0,030	8,57	3,971	+0,018
3,953	—	0,050	8,69	4,032	+0,079
3,953	—	0,080	8,81	4,087	+0,134

TABLE 3

Determination of Thorium in the Presence of the Rare Earths

Taken, mg		0.002 M Complexon III solution used, ml	Th found, mg	Absolute error, mg
Th	total			
3,953	2,096	8,60	3,990	+0,037
3,953	5,200	8,50	3,944	—0,009
7,906	7.860	17,00	7,888	—0,018
3,953	12,620	8,50	3,948	—0,005
3,953	34,500	8,53	3,981	+0,028

TABLE 4

Complexonometric Titration of Thorium after its Removal from Accompanying Metals

Taken, mg					Th found, mg	Absolute error, mg
total rare earths	Fe	Ti	Zr	Th		
15,0	50,0	2,0	0,438	1,976	1,972	—0,004
8,0	50,0	1.0	1,449	7,906	8,004	+0,098
8,0	50,0	1,0	1,449	3,953	4,060	+0,107
8,0	25,0	1,0	1,449	3,953	3,944	—0,009
12,0	25,0	1,0	1,41	5,929	6,032	+0,103
12,0	75,0	2,0	2,41	7,906	7,842	—0,064
8,0	50,0	1,5	2,50	3,953	4,018	+0,065
8,0	50,0	1,5	2,50	5,929	5,915	—0,014
10,0	25,0	10,0	5.0	1,430	1,324	—0,106
10,0	3,0	5.0	35,0	1,430	1,370	—0,060
10,0	3,0	3,0	25,0	2,840	2,900	+0,060
10,0	1,0	27,0	5,0	1,430	1,400	—0,030
10,0	1,0	21,0	5,0	2,840	2,790	—0,050

until the pH was 5 (congo red paper). The volume of the solution was made up to 50 ml with water and 7.5 ml of solution of acetonedioxalic acid added; the subsequent procedure followed was that described in [12]. Thorium was determined complexonometrically or photometrically in the solution obtained.

TABLE 5

Photometric Determination of Thorium after Its Separation from Accompanying Metals by the Iodate and Oxalate Methods

Taken, mg					Th found, mg	Absolute error, mg
total rare earths	Fe	Ti	Zr	Th		
10	2,0	—	31	0,020	0,018	—0,002
10	3,0	1,0	24,0	0,012	0,015	+0,003
10	25,0	10,0	10,0	0.050	0,044	—0,006
10	12,0	22,0	1,0	0.100	0,097	—0,003
10	12,0	16,0	—	0,208	0,195	—0,013
10	6,0	30,0	5,0	0,343	0,358	+0,015

TABLE 6

Complexonometric Determination of Thorium in Natural Materials

Designation of material	Thorium found (%) by:		Error (relative), %
	complexonometric method	control method	
Monazite I	2,31; 2,18	2,20	+2,2
The same II	1,72; 1,67	1,70	0,0
" " III	6,76; 6,54	6,44	+3,3
" " IV	3,20	3,28	−2,5
" " V	9,61; 9,88	9,80	+0,5
" " VI	2,55	2,65	+4,0
Winkite 1	0,69	0,68	+1,5
The same 2	1,28	1,32	—3,0
" " 3	1,44	1,35	+6,0
Zircon I	1,70	1,73	+1,8
The same II	1,36	1,30	+4,6
Ferrithorite	12,37	12,00	+3,0
Klopinite	2,56; 2,36	2,44	+0,8

Complexonometric and Photometric Method of Determining Thorium. To 10-15 ml of the test solution was added 1 ml of a 30% solution of potassium thiocyanate (ammonium). In the presence of iron the color of ferric thiocyanate appears; this acts as an indicator during titration.

In another 50 ml flask a compensating solution was prepared. For this purpose, the same amount of water was added, followed by 2 drops of hydrochloric acid, and 1 ml of potassium thiocyanate (ammonium).

To the compensating solution was added 3 drops of ferric chloride solution (10 mg Fe in 100 ml). When the color of the ferric thiocyanate was more intense in the test solution, 1-2 drops of 0.001% ascorbic acid solution was added, and the colors of the solutions compared after 2-3 minutes.

The color of both solutions should be exactly the same; when the color differed, 1-2 drops of ferric chloride solution was added to the less intensely colored solution.

First the iron in the compensating solution was titrated with 0.002 M (or 0.005 M) Complexon III solution. This solution was heated to 60° and then titrated slowly, dropwise, until it was colorless. The buret reading gave the correction to be applied. The test solution was also heated to 60° and slowly titrated with 0.002 M Complexon III solution until it was colorless. Titration was repeated twice.

It is clear from Tables 4 and 5 that complexonometric titration of thorium, and its photometric determination after its removal from accompanying elements by the iodate and oxalate methods, give satisfactory results.

TABLE 7

Colorimetric Determination of Thorium in Minerals and Ores

Test material	Thorium found (%) by:		Error (relative), %
	given method	control method	
Ore (ZrO_2—6,0, TiO_2—8%)	0,13	0,12	+ 8,3
Ore (ZrO_2—8,0)	0,14	0.14	0,0
Silicate ore	0,01;0,009	0,01	0,0
The same	0,007	0,007	0.0
Zircon	0,12; 0,13	0,12	+ 4,0
Ilmenite	0,04	0,036	+11,0
Winkite 1	0,68	0,69	— 1,30
The same 2	1,32	1,28	+ 3,1
" " 3	1,36	1,44	— 6,0
Monazite	3,28	3,20	2,2

During the complexonometric determination of thorium in thorium minerals—monazites from various deposits, ferrothorite, winkites, and also in ores—the solutions should be freed even from traces of zirconium (test with alizarin in a strongly acid medium) and titanium (test with hydrogen peroxide).

The method gives completely satisfactory results (Table 6).

Photometric determination of thorium was carried out on materials with a complex composition, containing from 0.005 to 3-4% of thorium and up to 60-70% of zirconium and titanium. The determination was carried out by means of arsenazo in tartaric acid* by a method described earlier (Table 7).

SUMMARY

A study has been made of the complexonometric titration of thorium in solutions containing calcium, zirconium, titanium, and the rare earths, using ferric thiocyanate as indicator.

A titrimetric method has been developed for the determination of thorium in natural materials containing large amounts of zirconium and titanium, in which use is made of the iodate and oxalate methods of precipitation, and also of a colorimetric method for the determination of small amounts of thorium by means of arsenazo. Determination of thorium by these methods takes 8-12 hours.

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COMPLEXONOMETRIC DETERMINATION OF MOLYBDENUM AFTER ITS REDUCTION TO THE QUINQUEVALENT STATE

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Quinquevalent molybdenum reacts with disodium ethylenediamine-tetracetate (Complexon III) in the molar proportions of 2:1 [1]. The compound thereby formed has been prepared, and its composition established by analysis and by a photometric method. Our experiments have shown that the readily hydrolyzable quinquevalent molybdenum does not form a precipitate in the presence of excess Complexon III, even in a strongly alkaline medium. On titrating the excess Complexon III with a solution of a zinc salt in the presence of chromogen black ET, a distinct color change is observed at the endpoint, and the color does not change on standing in air. All this indicates that the compound of quinquevalent molybdenum and Complexon III has a high stability.

We have shown previously [2] that the accuracy of the direct complexonometric titration of sexivalent molybdenum in the presence of pyrocatechol and indigocarmine as indicator, amounts to 2%; the color change at the endpoint is not clear enough, so that it is difficult in practice to titrate sexivalent molybdenum directly with Complexon III solution.

A review of complexonometric methods for the determination of sexivalent molybdenum is given in one of our previous articles [2].

The aim of the work described here was to establish the pH limits for the formation of the compound of quinquevalent molybdenum with Complexon III, and to establish the possibility of an indirect complexonometric determination of molybdenum after its conversion into the quinquevalent state.

A zinc or magnesium salt was used for determining the excess Complexon III.

EXPERIMENTAL

A solution of ammonium molybdate (chemically pure, GOST 3765-53) in water was standardized by the 8-hydroxyquinoline method [3]. 1 ml of this solution was found to contain 1.898, 1.890, 1.898, 1.891, and 1.886 mg of Mo (an average of 1.893 mg Mo/ml).

The Complexon III was purified by Bleadel and Knight's method [4], methanol being used instead of ethanol. An accurate aliquot of this material dried to constant weight was dissolved in water in a standard flask. The concentration of the solution was checked by means of solutions of zinc, cadmium, and magnesium of known concentration [5]; according to the results obtained, the molarities obtained were 0.008045 M according to Cd, 0.008050 M according to $MgSO_4$, and 0.008035 M and 0.008050 M with respect to Zn; the average value was 0.008050 M.

Hydrazine hydrochloride was used without further purification for reducing sexivalent molybdenum. Other reducing agents proved to be less suitable.

The indicator was prepared by triturating one part of chromogen black ET with 200 parts of sodium chloride. A buffer solution with a pH of 10 was prepared by adding 70 g of ammonium chloride to 570 ml of a concentrated ammonia solution (sp. gr. 0.90) and diluting to 1 liter with water [5].

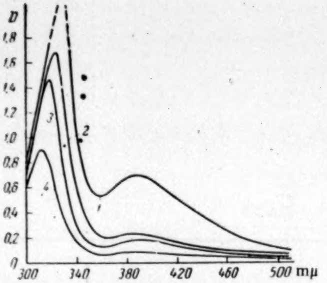

Fig. 1. Absorption curves for solutions of a quinquevalent molybdenum salt, and of the compound of quinquevalent molybdenum with Complexon III. SF-4 spectrophotometer. Cuvette with a layer thickness of 1 cm. All the curves were taken relative to water. 1) Mo^V ($4.032 \cdot 10^{-3}$ M) + Complexon III ($4.044 \cdot 10^{-3}$ M) in 0.24 M HCl, pH 2.17-9.30; 2) Mo^V ($4.032 \cdot 10^{-3}$ M) in 0.24 M HCl, Mo^V ($4.032 \cdot 10^{-3}$ M) + Complexon III in 2.0 M HCl; 3) Mo^V ($1.008 \cdot 10^{-3}$ M) + Complexon III ($1.011 \cdot 10^{-3}$ M) in 0.48 M HCl; 4) Mo^V ($1.008 \cdot 10^{-3}$ M) in 0.48 M HCl.

TABLE 1

Molar Extinction Coefficients of the Compound of Mo^V with Complexon III at Various Acidities (Determined at 387.5 mμ. Calculated on the basis of the Molar Concentration of Mo)

Acidity of the sol., pH	Molar coefficient	Acidity of the solution, M HCl	Molar coefficient
9,30	108		
9,08*	116	0,24	120
9,10*	115	0,24	115
8,70*	108	0,48	115
7,89	115	0,48	116
7,81	115	0,48	111
6,80	116	0,75	92
5,33	116	0,96	64
2,67	119	1,44	14
1,81	115	1,92	4.5
1,48	117		

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*Solution obtained on standing in all cases of determination of quinquevalent molybdenum indicated.

Acidity Limits for the Formation of the Compound of Quinquevalent Molybdenum with Complexon III. The acidity limits within which the compound of quinquevalent molybdenum and Complexon III is formed, were established by a photometric method.

When excess Complexon III is added to the brownish-yellow solution of quinquevalent molybdenum, the solution becomes a bright green, both in acid and alkaline media. This leads one to suppose that the complex compound of quinquevalent molybdenum is formed over a wide range of acidities.

The absorption curves for the quinquevalent molybdenum salt $(NH_4)_3MoOCl_6$ on its own, and for the compound of quinquevalent molybdenum with Complexon III, at varying acidities of the solution, are shown in Fig. 1. The curve for $(NH_4)_3MoOCl_6$ has two maxima: one—the larger one—at 310 mμ, the other—the smaller—at 375 mμ. Curve 1 also has two maxima, but their heights are somewhat greater (for the same concentration of quinquevalent molybdenum), the maxima in this case being shifted towards the longer wavelengths; one is located at 317.5 and the other at 387.5 mμ.

At a hydrochloric acid concentration of 2.0 M HCl, in the presence of excess Complexion III, the absorption curve almost coincides completely with the absorption curve of the solution of the quinquevalent molybdenum salt (Fig. 1, Curve 2).

Thus, in 2.0 M HCl, quinquevalent molybdenum does not form a compound with Complexon III. In order to establish with greater accuracy the acidity limits within which formation of the complex with Complexon III occurs, the molar extinction coefficients of quinquevalent molybdenum in the presence of excess Complexon III were determined at various acidities. 19.34 mg of sexivalent molybdenum was reduced to the quinquivalent state as described below (during this operation the volume is reduced by one half). To the solution with the highest concentration of acid was added 20 ml of 0.01 M Complexon III solution, and the acidity adjusted to the requisite level by addition of hydrochloric acid or ammonia; the solution was then boiled, after cooling, its volume was made up to 50 ml with water and its pH measured by means of a pH meter with a glass electrode, or a calculated amount of acid was added. For acidities ranging from 0.24 to 2.0 M HCl, the zero solution used was a solution of a quinquevalent molybdenum salt of the same concentration at the corresponding acidity; while within the limits pH 1 to pH 9.30, a solution of a quinquevalent molybdenum salt with a pH of 1 was used, since at higher pH values hydrolysis of quinquevalent molybdenum occurs. These experiments showed that the optical densities of solutions of quinquevalent molybdenum differ little from each other at various acidities (for 19.34 mg of Mo^V in 50 ml, in 1 M HCl, D = 0.203; in 0.24 M HCl, D = 0.195; at pH = 1, D = 0.208). Thus

TABLE 2

Conditions for the Quantitative Reduction of Sexivalent Molybdenum by means of Hydrazine (18.93 mg Mo taken)

Conditions		Mo found, mg	Error	
			mg	%
HCl concentration, mole/liter	0,1*	—	—	—
	0,2**	18,60	— 0,33	— 0,74
	0,3	19.04	+ 0,11	+ 0,58
	0,4	18,85	— 0,08	— 0,42
	0,7	19.04	+ 0,11	+ 0,58
	1,0	19.12	+ 0,19	+ 1,00
	1,3	18.96	+ 0,03	+ 0,16
Amount of $N_2H_4 \cdot 2HCl$, mg	1	4.107	—14.82	—78,3
	5	16,15	— 2,78	—14,7
	10	18,88	— 0,05	— 0,26
	50	18,96	+ 0,03	+ 0,16
	100	18.73	— 0,20	— 1,06
	500	19,00	+ 0,07	+ 0,37
Duration of the reduction,*** minutes	0	12,28	— 6,65	—35,13
	1	16,65	— 2,28	—12,04
	2	18,85	— 0,08	— 0,43
	2	18,73	— 0,20	— 1,06
	5	19,00	+ 0,07	+ 0,37
	10	18,73	— 0,20	— 1,06
	20	18,96	+ 0,03	+ 0,16

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*Molybdenum blue formed.

**Small amount of molybdenum blue formed.

***The time was counted from the moment when all the molybdate solution had been added to the hydrochloric acid solution of hydrazine. When this time had expired the reaction mixture was cooled with cold water.

measurement of the optical density of solutions at various pH values, relative to a null solution of a salt of quinquevalent molybdenum with pH 1 should not lead to a large error.

It is clear from Table 1 that on heating, quinquevalent molybdenum forms a compound with Complexon III within a wide range of acidities, namely from 0.5 M HCl to pH 10; within this range the reaction of complex formation proceeds quantitatively. Formation of a compound at such a high acidity could be of undoubted practical interest for the analytical chemistry of molybdenum were it possible to find a suitable complexonometric indicator, since most elements do not give a compound with Complexon III at such an acidity, and the reaction would appear to be selective.

As far as one can judge, quinquevalent molybdenum reacts with Complexon III fairly rapidly in hot acid solutions. At room temperature, in a medium of 0.5 M HCl, the reaction proceeds slowly.

For lack of an indicator for quinquevalent molybdenum it was complexonometrically determined by an indirect method at a pH of 10.

Conditions for the Reduction of Sexivalent Molybdenum to the Quinquevalent State by Means of Hydrazine. A study was made of the effect of acid concentration, the amount of hydrazine, and the duration of the reaction on the extent to which the sexivalent molybdenum is reduced.

The results (Table 2) show that the acid concentration during reduction should be higher than 0.3 M, otherwise, molybdenum blue is formed which interferes with titration. The amount of hydrazine hydrochloride should be greater than 10 mg per 40 ml of solution; when smaller amounts are used the sexivalent molybdenum is incompletely reduced. It is quite sufficient to boil the solution for 2 minutes.

When hydrazine is added to a cold, weakly acid solution of molybdate, or molybdate solution is added rapidly to a hot acid solution of hydrazine, molybdenum blue is formed which interferes with the titration. For

TABLE 3

Determination of Quinquevalent Molybdenum by Titration of Excess Complexon III with a Zinc Salt in the Presence of Chromogen Black ET-00

Mo, mg		Error		Mo, mg		Error	
in mg	%	in mg	%	in mg	%	in mg	%
113,6	113,1	—0,50	—0,44	18,9	18,9	0,0	0
75.72	75,58	—0,14	—0,18	18.9	18,9	0,0	0
75,72	75.53	—0,12	—0,16	18,9	18,8	—0,1	—0,43
37,86	38,07	+0,21	+0,55	9,46	9,56	+0,1	+0,97
37.87	38.24	+0,38	+1.00	9,46	9,38	—0,08	—0,86
37,86	37.94	+0,08	+0.21	3,79	3,95	+0,16	+4,4
28,40	28,54	+0,14	+0,49	1,89	1,80	—0,09	—4,7
28,40	28,34	—0,06	—0,21	1,89	2,05	+0,16	+8,4
18,9	19,0	+0,1	+0,4				

TABLE 4

Determination of Quinquevalent Molybdenum without Boiling (18.9 mg Mo taken)

Found, mg	Error		Found, mg	Error	
	in mg	in %		in mg	in %
18,1	—0,8	—4,2	18,7	—0,2	—1,1
18,3	—0,6	—3,2	18,7	—0,2	—1,2
17,7	—1,2	—6,2	18,6	—0,3	—1,6
18,7	—0,2	—1,1	18,6	—0,3	—1,7
18,7	—0,2	—1,1	18,5	—0,4	—2,4
18,6	—0,3	—1,6	18,3	—0,6	—3,2
18,8	—0,2	—0,9	17,9	—1,0	—5,3

reducing sexivalent molybdenum, it is best to add the test solution (10 ml) containing 10-100 mg of molybdenum, slowly, dropwise, to the hot, acid solution of hydrazine hydrochloride. When this technique is used no molybdenum blue is formed. Should some molybdenum blue still appear, further boiling will usually lead to its disappearance.

Determination of Quinquevalent Molybdenum by Titration with Complexon III, Excess of which is Determined by means of a Zinc Salt and Chromogen Black ET-00. After many preliminary experiments the following method was developed for determining molybdenum. In a 200 ml beaker is placed 2-5 ml of hydrazine hydrochloride solution (concentration 0.01 g/ml), and 1-3 ml of concentrated hydrochloric acid and the volume made up to 30 ml with water; the solution obtained is heated to the boil on an electric hotplate, when not more than 10 ml of the neutral or weakly acid test solution of molybdate, containing from 10 to 100 mg of Mo, is added, slowly, dropwise; boiling is continued for several minutes until the solution is yellow-brown in color. To this solution is added a known volume of 0.01 M Complexon III solution whose concentration is accurately known, and some of the mixture of chromogen black ET-00 with sodium chloride added on a spatula tip. The acid solution is neutralized with ammonia or NaOH until the yellow color of the solution changes to weak green; finally for each 100 ml of solution, 2 ml of the buffer solution with pH 10 is added, and the whole boiled. After cooling to 40-60° the solution should be bright green in color. If this is not the case a little more indicator should be added. The hot (40-60°) solution is titrated with 0.01 M zinc sulfate solution until the bright green color changes to red-brown on addition of one drop of titrant. For calculation it is assumed that quinquevalent molybdenum reacts with Complexon III in the molar ratio of 2 : 1.

Results of molybdenum determinations are given in Table 3. They show that the method has satisfactory accuracy. When this procedure is adopted, however, the conditions employed for reducing the sexivalent molybdenum must be strictly adhered to in order to avoid formation of molybdenum blue. If the latter should appear,

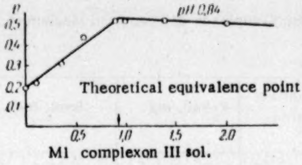

Fig. 2. Curves for the direct spectro-photometric titration of quinquevalent molybdenum with a solution of Complexon III.SF-4 spectrophotometer, cuvette with a layer thickness of 1 cm. Wavelength 387.5 mμ. 4.352 mg of M Mo^V taken; 0.915 ml of 0.02486 M Complexon III used. 4.365 mg of Mo found. The curves taken at pH 0.84, 1.15, and 1.80 almost coincided.

even if only in small amounts, the acidity of the solution should be raised and the solution boiled for a prolonged time, or even until the solution has been evaporated almost to dryness.

On neutralizing an acid solution of quinquevalent molybdenum containing excess Complexon III, a turbidity sometimes appears (as a result of the hydrolysis of Mo^V), this, however, disappears on heating.

Experiments showed that if the solution of quinquevalent molybdenum and excess Complexon III is not heated before titration, and is not titrated at 40-60°, then low results are obtained (Table 4).

Determination of quinquevalent molybdenum by titration of excess ComplexonIII with zinc sulfate solution in the presence of chromogen black ET-00 as indicator, takes a comparatively short time. It can be carried out in half an hour. The error in determining 10-100 mg of Mo is ± 0.5%, i.e., this method ensures slightly more accurate results than was possible by the direct titration of sexivalent molybdenum with Complexon III in the presence of pyocatechol and indigocarmine [2].

The test solution should be free from tartrates, citrates, oxalates, nitrates, and nitrites as well as other oxidizing agents. Iron interferes.

Small amounts of tungsten (10 mg of W per 40 ml) do not interfere with molybdenum determination. During reduction of molybdenum in the presence of tungsten a little of the blue compound is formed, but, on prolonged boiling in 0.7 M HCl a dirty blue compound is precipitated (contaminated tungstic acid) which dissolved in alkali. The blue compound disappears in the presence of excess Complexon III in an alkali medium on heating, and satisfactory results are obtained for molybdenum. When larger amounts of tungsten are present the blue compound does not disappear completely, and interferes with the titration. The results obtained are given in Table 5.

Elements which normally titrate with Complexon III in an alkali medium in the presence of chromogen black ET-00 interfere with molybdenum determination. In such cases total quinquevalent molybdenum and the accompanying elements can be titrated first, and then, in another aliquot of the test solution, the accompanying elements are titrated without reducing the sexivalent molybdenum (the latter, under the titration conditions used, does not form a stable compound with Complexon III); the amount of molybdenum is determined by difference. Results for such determinations are given in Table 5.

TABLE 5

Determination of Molybdenum in the Presence of Foreign Ions

Taken, mg	Mo, mg		Error		Taken, mg	Mo, mg		Error	
	taken	found	in mg	in %		taken	found	in mg	in %
5 W	9.46	9,32	—0,14	— 1,48	100 W*	9,46	7,91	—1,56	—16,4
10 W	9.46	9,46	—0.00	— 0,07	26 Zn	18,9	18,8	—0,1	— 0,69
20 W*	9.46	9.25	—0,21	— 2,29	13 Zn	18,9	18,9	+0,0	+ 0,10
20 W	9,46	8,96	—0,50	— 5,32	5 Mg	18,9	18,8	—0,1	— 0,42
40 W	9.46	8,17	—1,29	—13,6	16 Ca	18,9	19,0	+0,1	+ 0,53
100 W	9,46	7,41	—2,05	—21,6	12 Ni	19,2	19,5	+0,2	+ 1,25

*The volume of the solution during reduction was 80 ml.

In the presence of Mg, and Ca, titration should be carried out with $MgSO_4$ solution, while NaOH or KOH should be used instead of NH_4OH for neutralizing the solution. The chromogen black ET-00 indicator should be added before titration; the acid solution is best neutralized using universal indicator paper.

TABLE 6

Spectrophotocolorimetric Titration of Quinquevalent Molybdenum with Complexon III in an Acid Medium (4.35 mg Mo taken; wavelength 387.5 mμ)

pH of the solution being titrated	Found, mg	Error, mg	pH of the solution being titrated	Found, mg	Error, mg
0.43	—	—	1.15	4.36	+0.01
0.66*	4.41	+0.06	1.72	4.22	-0.13
0.84	4.36	+0.01	1.80	4.15	-0.20
1.15	4.29	-0.06	1.80	4.17	-0.18

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*The optical density of the solution was measured after standing for a long time after addition of each new portion of Complexon III solution, since the reaction proceeds very slowly at pH 0.7.

Quinquevalent molybdenum can be determined by direct photometric titration with Complexon III solution in an acid medium at 387.5 mμ, by using a SF-4 spectrophotometer with a special cuvette having a layer thickness of 1 cm. The quinquevalent molybdenum solution was prepared as described above. The approximate pH value of the solution was measured with a pH-meter with a glass electrode. The volume of solution being titrated was 15 ml.

Although it has been established previously that even in 0.48 M HCl, Complexon III reacts quantitatively with quinquevalent molybdenum on heating, at such an acidity the titration cannot be carried out at room temperature, since the reaction proceeds slowly. It was established by photometric titration that at a pH of 0.66 the reaction finishes completely in half an hour, at a pH of 0.84 in 5 minutes, and at a pH of 1.80 in one minute. Direct titration at a pH > 2 is excluded since the quinquevalent molybdenum is hydrolyzed. Thus, direct titration of quinquevalent molybdenum is possible at pH 0.8-1.80. Under these conditions satisfactory results are obtained for molybdenum (Fig. 2, Table 6).

SUMMARY

The acidity limits within which the compound between quinquevalent molybdenum and Complexon III is formed have been established.

An accurate method has been developed for the determination of quinquevalent molybdenum, in which excess Complexon III solution is titrated with a zinc salt in the presence of chromogen black ET-00. It has been shown that it is possible to determine quinquevalent molybdenum by direct photometric titration.

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SPECTROPHOTOMETRIC STUDIES OF URANIUM SOLUTIONS

COMMUNICATION 2. A SPECTROPHOTOMETRIC METHOD OF DETERMINING URANIUM IN ORES AND OTHER MATERIALS AS THE THIOCYANATE AFTER EXTRACTION OF OF THE URANIUM WITH METHYL ETHYL KETONE*

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In a previous article [1] we have shown that direct determination of uranium on the basis of the value of the light absorption of uranyl nitrate in organic solvents is only applicable for fairly high concentrations of uranium. In order to increase the sensitivity of the determination of uranium, methods of extracting it in the form of inorganic and organic complexes [2-9] have been widely used. All the same, we think that it is better to start by extracting the uranium as its nitrate in an organic solvent (for separating it from most elements), and then determining it directly in the organic phase by a spectrophotometric method after addition of a suitable reagent. By using this technique, determination of uranium can be speeded up and simplified. After the work described here was completed (in 1954) a number of papers appeared which confirmed the advantages of such an approach for determining uranium [10-14].

We used methyl ethyl ketone for extracting uranyl nitrate; the partition coefficient of uranyl nitrate in this solvent is greater (K = 21) than in other organic solvents [1]. Ammonium thiocyanate was chosen as the reagent.

Measurements of the optical density were carried out on a SF-11 spectrophotometer using quartz cuvettes (layer thickness 1 cm) and were made relative to methyl ethyl ketone or a mixture of water and acetone containing all the reagents at the same concentrations as the test solution [15]. The uranyl nitrate solutions were prepared from high purity (99.7%) uranium metal. The uranyl sulfate was prepared from uranyl nitrate. Solutions of other salts were prepared from chemically pure or analytical grade reagents (the analytical grades were recrystallized). The methyl ethyl ketone and acetone were distilled.

Spectrophotometric Measurements of the Thiocyanate Complex of Uranium. In Fig. 1 (Curve 1) is shown the absorption curve of the uranium thiocyanate complex (2.1×10^{-4} M) in an aqueous acetone medium (60% acetone by volume). The molar absorption coefficients of the complex in this medium are: 6200, 3600, and 1300 at 350, 375, and 400 mμ respectively.

The effect of Fe, Cu, Al, Ti, V, and Mo (see also [16]) on the value of the light absorption of the uranium thiocyanate complex was studied. To a solution of uranyl sulfate, containing 0.5 mg of uranium, was added the sulfates of the elements listed above (V in the form of vanadate, Mo as the molybdate), 0.4 ml of 10% stannous chloride in hydrochloric acid (1:1) (for reducing Fe^{III}), 0.2 ml of concentrated H_2SO_4, and 6 ml of a saturated solution of ammonium thiocyanate in acetone, and the volume made up to 10 ml with water; the optical density of the final solution was measured after a few minutes.

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*A brief report of the material given in this article was given by P. N. Palei at the International Conference on the Peaceful Uses of Atomic Energy in Geneva in 1955, Reports of the Soviet Delegation at the International Conference on the Peaceful Uses of Atomic Energy "Research in the Fields of Geology, Chemistry, and Metallurgy," Acad. Sci. USSR Press, Moscow-Leningrad, 1955, p. 21.

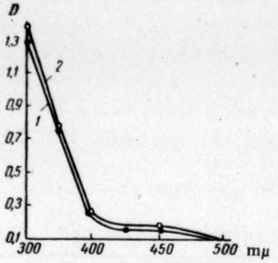

Fig. 1. Absorption curves for the uranium thiocyanate complex in an aqueous acetone medium (60% acetone by volume) (Curve 1), and in a mixture of methyl ethyl ketone and acetone (60% acetone by volume) (Curve 2). Uranium concentration 2.1×10^{-4} M.

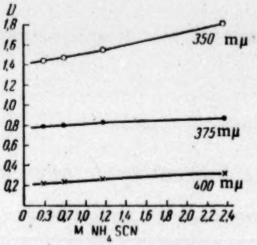

Fig. 2. Relation between the optical density of solutions of the uranium thiocyanate complex in methyl ethyl ketone—acetone mixtures (60% acetone) and thiocyanate concentration. Uranium concentration 2.1×10^{-4} M.

We found that small amounts of iron and copper (molar ratios of Fe and Cu to U of the order of 5 and 20 respectively) do not affect the optical density of the uranium thiocyanate complex in an aqueous acetone solution, when the measurements are made at 350 mμ. At a molar ratio of copper to uranium of 35, the optical density of the solution cannot be determined. Aluminum does not interfere with uranium determination even for large amounts of the former (Al_{mol}/U_{mol}) = 180) whatever wavelength is chosen for measuring the optical density of the solution of the uranium thiocyanate complex. The effect of small amounts of lead, cobalt, niobium, and molybdenum has already been noted in the literature [16].

Accordingly, the aqueous acetone medium can be used for the accurate quantitative spectrophotometric determination of uranium as its thiocyanate complex only after removing the uranium from a number of elements. In Fig. 1 (Curve 2) is shown the absorption of the uranium thiocyanate complex (uranium concentration 2.1×10^{-4} M) in a mixture of methyl ethyl ketone and acetone after quantitative extraction of uranium as its nitrate. This curve is similar to the absorption curve for the uranium thiocyanate complex in the aqueous acetone medium. The molar absorption coefficients(ϵ) of the uranium thiocyanate complex in the mixture of these solvents are somewhat greater than in the aqueous acetone medium and are equal to 6640, 3700, 1350, at 350, 375 and 400 mμ respectively.

The thiocyanate concentration has some effect on the light absorption of the uranium thiocyanate complex, particularly at 350 mμ (Fig. 2). This is connected, presumably, as in the case of aqueous solution, with a decrease in the dissociation of the uranium thiocyanate complex in the presence of large amounts of thiocyanate [17].

The color of the uranium thiocyanate complex develops rapidly, and the optical density is almost independent of the time for which the solution is allowed to stand, if the measurements are made at 375 and 400 mμ, while it increases at 350 mμ after being allowed to stand for 40 minutes (Fig. 3).

For the uranium concentrations examined (4.2×10^{-5} - 6.3×10^{-4} M) the solutions conform to the Bouger-Beer law for all the wavelengths* indicated (Fig. 4).

A study was made of the effect on the light absorption of the uranium thiocyanate complex of those elements, which either give colored compounds with thiocyanate (Fe, Cu, Co, Bi, Ti, and Mo) or possess an intrinsic color (e.g.,V). Solutions of salts of these elements were added before the extraction to a saturated solution of ammonium nitrate containing uranyl nitrate.

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* A few crystals of ascorbic acid were added to these solutions.

TABLE 1

Spectrophotometric Determination of Uranium as its Thiocyanate Complex, after Extraction with Methyl Ethyl Ketone from Solutions Containing Other Elements and Masking Agents (the amount of uranium taken in each case was 0.50 mg*)

Element added	Molar ratio of element to uranium	Optical density for the following wave length in mμ			Uranium obtained in mg at the following wavelength in mμ			Relative error in % at the following wavelength in mμ			Notes
		350	375	400	350	375	400	350	375	400	
U	—	1,40	0,78	0,27	—	—	—	—	—	—	Ascorbic acid added
U+Fe	43	1,40	0,78	0,27	0,50	0,50	0,50	0	0	0	The same
U+Fe	860	1,40	0,78	0,27	0,50	0,50	0,50	0	0	0	» »
U+Cu	38	1,40	0,77	0,28	0,50	0,495	0,505	0	—1,0	+1,0	» »
U+Cu	380	1,47	0,80	0,28	0,52	0,52	0,505	+4,0	+4,0	+1,0	» »
U+Co	40	1,40	0.79	0,28	0.50	0,505	0,505	0	+1,0	+1,0	» »
U+Co	400	1,42	0,79	0,28	0,505	0,505	0,505	+1,0	+1,0	+1,0	» »
U	—	1,40	0,62	0,20	—	—	—	—	—	—	Lactic acid added
U+Mo	25	1,38	0,61	0,20	0,49	0,49	0,50	—2,0	—2,0	0	The same
U+Zr	52	—	0,935	0,31	—	—	—	—	—	—	Zirconium nitrate added
U+Zr+V	Zr/U=52 V/U=50	—	0,927	0,315	—	0,497	0,503	—	—0,6	+0,6	The same
U+Zr+V+Fe+Cu+Co	Zr/U=52; V/U=50 Fe/U=43; Cu/U=38 Co/U=40		0,925	0,315	—	0,495	0,503	—	—1,0	+0,6	» »
U+Mo+V+Fe+Cu+Co	Mo/U=25; V/U=50 Fe/U=43; Cu/U=38 Co/U=40		0,93	0,32	—	0,498	0,505	—	—0,4	+1,0	With re-extraction and subsequent addition of zirconium nitrate

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*Each figure is the mean of five determinations.

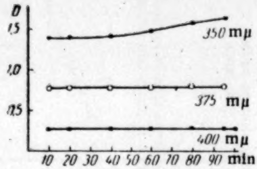

Fig. 3. Relation between the optical density of solutions of the uranium thiocyanate complex in mixtures of methyl ethyl ketone and acetone (60% acetone), and the time interval between formation of the complex and measurement of the density. Uranium concentration 2.1 × 10^{-4} M.

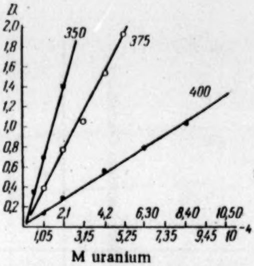

Fig. 4. Relation between the optical density of solutions of the uranium thiocyanate complex in methyl ethyl ketone–acetone mixtures (60% acetone) and uranium concentration.

As the experiments showed, the presence of Fe^{III}, Cu^{II}, Bi, Ti^{IV} in the solution prior to extraction, led to an increase in the optical density of the uranium thiocyanate complex in the organic layer; this indicates partial extraction of these elements by methyl ethyl ketone. Molybdenum depresses the optical density of the uranium thiocyanate complex in the same way as it does in an aqueous acetone medium. Apparently, molybdate ions partially complex uranium as a poly compound.

For suppressing the effect of small amounts of Fe^{III}, Cu^{II}, and Co^{II} extracted by the methyl ethyl ketone, it proved sufficient, as experiments showed, to add a few crystals of ascorbic acid to the uranium thiocyanate complex in the methyl ethyl ketone – acetone mixture. When this technique is adopted the optical density of the uranium thiocyanate complex does not change (Table 1). We tried to eliminate interference on the part of V^V and Mo^{VI} by modifying the extraction conditions (adding reducing agents to the solution: $SnCl_2$, ascorbic acid, hydrazine sulfate; changing the pH; and adding Complexones I and III as masking agents [18]). Nevertheless, there was observed in all cases, either low (in the presence of Mo) or high (in the presence of V) values of the optical density of the uranium thiocyanate complex in the organic layer. It is of interest to note that in the presence of Complexon I, uranium is incompletely extracted by methyl ethyl ketone, while in the presence of Complexon III it is not extracted at all, although it is known that uranium forms compounds which have a low stability with these complexons [19]; we also confirmed this fact by a polarographic method. We established that by complexing the molybdenum, prior to extraction, as its complex with lactic acid*, its effect on the extraction of uranium with methyl ethylketone and on the subsequent measurement of the optical density of the uranium thiocyanate complex, could be completely eliminated (Table 1). Nevertheless, when such a technique is used, there is some decrease in the optical density of the uranium thiocyanate complex at 375 and 400 mμ (Table 1). Accordingly, in order to prepare calibration curves, it is necessary prior to extraction to add 1 ml of a 40% solution of lactic acid to the solution to be extracted.

The effect of vanadium cannot be removed by addition of lactic acid; V^V is reduced by lactic acid to V^{IV} or V^{III} (depending on temperature and duration of reduction), which absorb appreciably at 350-400 mμ [15]. Accordingly, zirconium nitrate ** was added to the solution to be extracted in order to complex the vanadium. When this technique is used, although the optical density of the uranium thiocyanate complex in the organic layer thereby increases, (this indicates partial extraction of zirconium nitrate by the methyl ethyl ketone), the optical density nevertheless remains constant whatever the amount of vanadium in the solution being extracted. Accordingly,

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*To 9 ml of a saturated solution of ammonium nitrate containing uranyl nitrate and ammonium molybdate, was added 1 ml of a 40% solution of lactic acid.

**1 ml of a 4.7% solution of $Zr(NO_3)_4 \cdot 5H_2O$ was added to 9 ml of solution.

TABLE 2

Determination of Uranium in Ores*

Sample No.	By the spectrophotometric method in %, at mμ: 375	By the spectrophotometric method in %, at mμ: 400	By a volumetric method, %	Difference in %, at mμ: 375	Difference in %, at mμ: 400
1	0,105	0,108	0,105	—	+0,003
2	0,91	0,87	0,87	+0,04	—
3	0,285	0,285	0,288	—0,003	—0,003
4	0,325	0,330	0,325	—	+0,005
5**	0,090	0,090	0,085	+0,005	+0,005
6	0,270	0,270	0,270	—	—

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*Each figure is the mean of six determinations; the deviation of individual results from the mean does not exceed ± 3%.

**Weight ratio of V:U = 10:1.

for the analysis of materials containing uranium and vanadium (and also Fe, Cu, and Co) it is necessary to construct calibration curves by adding to the standard solutions which are to be extracted, 1 ml of a 4.7% solution of zirconium nitrate; the light absorption of the uranium thiocyanate complex should be measured at 375 and 400 mμ when zirconium is present, since at 350 mμ zirconium interferes strongly.

When both molybdenum and vanadium are present in the test material (as well as Fe, Cu, and Co) it is not enough merely to extract the uranyl nitrate with methyl ethyl ketone, since the simultaneous addition of lactic acid (in order to complex the molybdenum), and zirconium nitrate (to complex the vanadium) to the test solution, leads to the formation of a bulky colloidal precipitate of zirconium lactate. In such cases satisfactory results can be obtained by using an intermediate re-extraction of the uranium with ammonium carbonate solution. First of all, the uranium is extracted with methyl ethyl ketone from a saturated solution of ammonium nitrate to which has been added 1 ml of a 40% solution of lactic acid (per 10 ml). Uranium is then re-extracted from the organic layer by a three fold treatment with 3 ml of 2% ammonium carbonate solution. The carbonate solution is evaporated to dryness and the residue calcined in a muffle at 500-600° * for 10-15 minutes; on cooling, the residue is dissolved in 2-3 ml of HNO_3(sp. gr. 1.39). The solution is evaporated to dryness and the residue dissolved in 9 ml of a saturated solution of ammonium nitrate, 1 ml of a 4.7% solution of zirconium nitrate is added and the uranium extracted twice with 2 ml lots of methyl ethyl ketone; the extracts are collected in a 10 ml standard flask, 6 ml of a saturated solution of ammonium thiocyanate in acetone is added, and the volume made up to the mark with methyl ethyl ketone. Ascorbic acid should not be added in this case, since it enhances the light absorption of the uranium thiocyanate complex in the final solution should the test material contain molybdenum and vanadium.

Calibration curves should be constructed by measuring the light absorption of standard solutions prepared in exactly the same way.

As a result of the work carried out, several variants of the method can be suggested which are based on extraction of the uranium with methyl ethyl ketone, with subsequent spectrophotometric determination of the uranium as its thiocyanate complex.

The first variant is applicable in the absence of Mo, V, Ti, and Bi, and in the presence of iron, copper, cobalt, and other elements in the test material. Uranium is extracted as uranyl nitrate from a solution, which is saturated with respect to ammonium nitrate, by means of methyl ethyl ketone; the thiocyanate complex of uranium* is obtained in the ketone phase, and the optical density of the solution is measured after addition of a few crystals of ascorbic acid (for eliminating the effect of traces of Fe^{III}, Cu^{II}, and Co^{II}).

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*When calcining is omitted high results are obtained.

**Analytical grade ammonium thiocyanate should be used, and material taken from the same supply or bottle should be used for the analysis and for constructing the calibration curves.

It takes 20-30 minutes to carry out an analysis by this variant, without taking into account the time taken to get the material into solution. The experimental accuracy is 1-2% relative.

The second variant is applicable in the presence of Mo, Fe, Co, Cu, and other elements, but in the absence of V and Ti, and differs from the first variant only in that, prior to extraction, 1 ml of 40% lactic acid solution is added to the test solution in order to complex the molybdenum. The time taken to carry out an analysis and the accuracy are the same as for the first variant.

The third variant is applicable in the presence of V, Fe, Co, Cu, and other elements, but in the absence of Mo, and differs from the first and second variants only in that, prior to extraction, 1 ml of a 4.7% solution of zirconium nitrate is added to the solution to complex vanadium.

The fourth variant is applicable when the sample contains Fe, Cu, Co, V, Mo and other elements and differs from all the other variants, in that an intermediate stage of reextraction of the uranium is used. From the methyl ethyl ketone layer, after the first extraction, (in the presence of lactic acid) the uranium is reextracted three times by means of a 2% solution of ammonium carbonate (5 ml each time); the solution is evaporated to dryness, and the residue calcined in a muffle, it is then dissolved in HNO_3, the solution is saturated with ammonium nitrate and zirconium nitrate solution is added, the uranium is then extracted again with ketone. A solution of ammonium thiocyanate in acetone is added to the methyl ethyl ketone phase and the light absorption measured. This variant of the method takes 3-4 hours. The accuracy is 1.5-2% relative.

Table 2 contains results of determinations of uranium in six samples of ore in which the content of this element had been established by chemical methods. The first five samples were analyzed by the third variant, while sample six was analyzed by the fourth variant. The method gives satisfactory results.

SUMMARY

Conditions have been established for the spectrophotometric determination of uranium in the form of its thiocyanate complex (after extraction of uranium as uranyl nitrate by means of methyl ketone) in samples which contain Fe, Cu, Co, V, Mo, and other elements.

The spectrophotometric method permits determination of 0.01-1.0% of uranium in ores (and other materials). The relative error is ± 2-3%.

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DETERMINATION OF URANIUM BY THE FLUORIDE METHOD WITH A FINAL TITRIMETRIC DETERMINATION*

V. M. Zvenigorodskaya and M. I. Ryanicheva

In 1948, while studying the phenomena which occur in solutions containing hydrofluoric acid, divalent iron, and salts of sexivalent uranium, we became aware that divalent iron is capable, under these conditions, of quantitatively reducing uranium to the quadrivalent state. In acid media, in the absence of fluoride ions, trivalent iron oxidizes quadrivalent uranium:

$$UO^{2+} + 2Fe^{3+} + H_2O \rightarrow UO_2^{2+} + 2Fe^{2+} + 2H^+. \qquad (1)$$

Auger's method [1], for example, which was checked and confirmed recently by Weiss and Blum [2], is based on this reaction. Trivalent iron is added as a catalyst to the solution of quadrivalent uranium during its titration with dichromate [3].

Depending on the hydrofluoric acid concentration, the oxidation–reduction potentials of the system U^{VI}/U^{IV} and Fe^{III}/Fe^{II} changes, the potential of the system U^{VI}/U^{IV} increases strongly, while the potential of the system Fe^{III}/Fe^{II} drops appreciably (Fig. 1); at the point where the hydrofluoric acid concentration is 2-3 moles/liter, the potential of the system Fe^{III}/Fe^{II} becomes 0.17-0.20 volt more electronegative than the potential of the system U^{VI}/U^{IV}. In practice, such a potential difference is sufficient to ensure that the following reaction can proceed:

$$UO_2^{2+} + 2Fe^{2+} + 4H^+ + 16F \rightarrow UF_4 + 2[FeF_6]^{3-} + 2H_2O \qquad (2)$$

According to our results, the latter reaction occurs within a very wide range of hydrogen ion concentration, starting at a pH of 4-5.

On the basis of this principle we have developed two rapid methods for the determination of uranium [5]. One of them which was designed for the determination of small amounts of uranium with a photometric finish was published recently [6], the other, with a titrimetric finish is described below.

Some of the Properties of the Simple and Double Fluorides of Quadrivalent Uranium

Despite a widely held opinion [7], the fluoride of quadrivalent uranium is appreciably soluble in hydrofluoric acid [8] and cannot be used for the quantitative determination of uranium. As long ago as 1936, Khlopin and Gerling [9] came to the conclusion that the double fluoride of quadrivalent uranium and ammonium is considerably less soluble than the simple fluoride of uranium, and suggested precipitating quadrivalent uranium in an acetate buffer medium in the presence of excess ammonium fluoride.

However, according to our results (1949), of the double compounds of uranium (IV) fluoride with the alkali metals**, only the double fluoride of uranium (IV) and sodium has a sufficiently low solubility and is precipitated

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*This work was carried out in 1948-1952.

** The following double fluorides were examined: uranium(IV)-sodium, uranium (VI)-calcium, uranium (IV)-ammonium, and uranium (IV)-lithium.

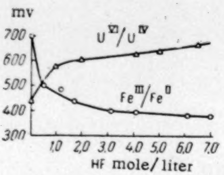

Fig. 1. The actual potential of the systems U^{VI}/U^{IV} and Fe^{III}/Fe^{II} as a function of the hydrofluoric acid concentration in 1 N sulfuric acid.

almost completely, not only in an acetate buffer, but also in a mineral acid medium. Its solubility in an n-molar solution of hydrofluoric acid (n = 1, 2, 3, 4) containing sulfuric acid at concentrations from 0.01 to 1 N, and from 2 to 10% sodium sulfate, amounts to 0.1-0.15 mg of U in 100 ml. In the presence of excess sodium salts, e.g., at U:Na = about 1:10 and 1:40, in solutions of hydrofluoric acid containing sulfuric acid, the same anhydrous compound $NaUF_5$ is always formed. It crystallizes in the hexagonal crystal system, but with different parameters for the elementary cell:

$$a = 4{,}47 \pm 0{,}05\text{A}, \quad c = 7{,}24 \pm 0{,}05\text{A} \text{ and } a = 4{,}17 \pm 0{,}05\text{A}, \quad c = 6{,}76 \pm 0{,}05\text{A}.$$

The difference between the completeness of precipitation of simple uranium (IV) fluoride and its double fluoride $NaUF_5$ can be illustrated by the determination of uranium (IV) in a sample of synthetic pitchblende (sample 466). The determination was carried out twice; first, the fluoride was isolated by a generally accepted procedure [7], i.e., from a solution containing 5-10 ml of hydrofluoric acid in 100 ml of solution, the second time it was isolated by the same procedure, but with the modification that during the treatment of an aliquot with hydrofluoric acid in a platinum basin, 2 g of sodium sulfate was added. The difference between the results was very great: When no sodium sulfate was used 3.88% U was found, while when sodium sulfate was used the amounts found were 27.48 and 27.02% U.

The experimental results (Table 1) clearly demonstrate the very close relation between completeness of precipitation of the double fluorides of uranium (IV) and the nature of the cation. The fluorides were isolated after reduction of uranium with divalent iron under the following conditions: in experiments 1-6, 5.0-5.5 ml of sulfuric acid 1:1, 2 g of Mohr's salt, 10 ml of 40% hydrofluoric acid, and 2 g of sodium sulfate were added to a known volume of a weakly acid standard solution of uranyl sulfate, the final solution was diluted with water to 100 ml; the sulfuric acid concentration thereupon is lowered to about 1 N. The whole was thoroughly mixed and the precipitate allowed to stand overnight. The precipitate was filtered off and washed with wash liquor with a pH of about 2(50 ml of hydrofluoric acid + 40 g of ammonium acetate, and the volume made up to 1 liter with water) until the washings gave a negative reaction for divalent iron (test with orthophenanthroline or α,α'-dipyridyl). The residue was then titrated with 0.01 N vanadate solution using phenanthranilic acid as indicator.

In experiments 7-15, in order to simulate the conditions used by Khlopin and Gerlin [9], acetate was added instead of sulfuric acid until the pH was 1.6-2.0. In experiments 7-11, 4 g of sodium acetate was added in each case, while in experiments 12-15, in order to compare the effect of the cation, 5 g of ammonium acetate was added.

Experiments showed that even in an acetate medium, i.e., under those conditions indicated by Khlopin and Gerling [9], positive results are only obtained in the presence of sodium salts (compare experiments 7-11 with experiments 12-15). In addition to this, in experiments 1-6 in 1 N sulfuric acid, despite the presence of sodium salts, there is observed a systematic drop in the results on the average equal to 0.32 mg of uranium.

On this basis it would appear that in order to obtain complete precipitation of the double fluoride of uranium (IV) and sodium, the acetate buffer mixture is to be preferred. Nevertheless, it was found that the buffered medium is only suitable for the determination of uranium in pure solutions (e.g., in an uranium pitchblende), since at a relatively high pH, in addition to uranium there are precipitated the compounds of trivalent and divalent iron, quadri- and trivalent vanadium, calcium and magnesium fluorides, etc., as a result of which washing of the precipitate and the oxidimetric titration of uranium becomes impossible.

Thus, in order to determine uranium in mineral raw material by the fluoride method, we decided to use precipitation of the double fluoride $NaUF_5$ from a mineral acid medium, and apply some empirical corrections.

TABLE 1

Precipitation of Uranium (IV) in the Form of its Double Fluorides with Ammonium and Sodium in an Acetate or Mineral Acid Medium in the Presence of Hydrofluoric Acid

Test No.	0.01 N solution of U taken, ml	0.01 N NH_4VO_3 used, ml	Deviation			Added		
			0.01 N solution, ml	U, mg	in relative %	sodium acetate	ammonium acetate	sodium sulfate
1	22,13	21,86	−0,27	−0,33	− 1,3	—	—	2
2	22,13	21,79	−0,34	−0,40	− 1,5	—	—	2
3	22,13	21,87	−0,26	−0,30	− 1,2	—	—	2
4	17,44	17,22	−0,22	−0,26	− 1,2	—	—	2
5	17,44	17,20	−0,24	−0,28	− 1,3	—	—	2
6	17,44	17,15	−0,29	−0,34	− 1,6	—	—	—
	Mean		−0,27	−0,32	− 1,3			
7	12,69	12,67	−0,02	−0,02	− 0.1	4	—	—
8	12,69	12,64	−0,05	−0,06	− 0,4	4	—	—
9	12,69	12,64	−0,05	−0,06	− 0,4	4	—	—
10	12,69	12,67	−0,02	−0,02	− 0,1	4	—	—
11	12,69	12,69	±0,00	±0,00	± 0,0	4	—	—
	None		−0,03	−0,03	− 0,2			
12	22,13	16,07	−6,06	−7,21	−27,7	—	5	None
13	22,13	17,30	−4,83	−5,75	−22,1	—	5	—
14	22,13	17,48	−4,65	−5,53	−21,2	—	5	—
15	22,13	17,82	−4,31	−5,13	−19,7	—	5	—
	Mean		−4,96	−5,90	−22,7			

The Effect of Foreign Ions on the Determination of Uranium as the Double Fluoride of Uranium (IV) and Sodium in a Mineral Acid Medium

Uranium often turns up in ores and rocks. For its determination in mineral raw material, primary attention must be given to the behavior of vanadium.

The normal oxidation−reduction potentials of the systems U^{VI}/U^{IV} and V^{IV}/V^{III} are very close; the potential of U^{VI}/U^{IV} is equal to 0.407 ± 0.003 volt [10], while the potential of V^{IV}/V^{III} is equal to 0.337 volt [11]. Accordingly, it is almost impossible, in practice, to choose a reducing agent, which, while quantitatively reducing uranium to the quadrivalent state, does not, at the same time, reduce vanadium to the trivalent state, even if only partially. In an acid medium, divalent iron reduces quinquevalent vanadium to the quadrivalent state. But, in an acid medium in the presence of hydrofluoric acid, iron (II) reduces vanadium to the trivalent state in connection with the formation of a stable fluoride complex of trivalent vanadium, while the potential of the system V^{IV}/V^{III} increases so much that it becomes more electropositive than the potential of the system Fe^{III}/Fe^{II} (Fig. 2).

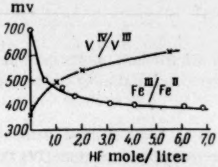

Fig. 2. The actual potential of the system Fe^{III}/Fe^{II} and V^{IV}/V^{III} in 1 N sulfuric acid as a function of hydrofluoric acid concentration.

The analogy between uranium and vanadium can be taken even further, namely the capacity of the tri- and quadrivalent compounds of vanadium to form double fluorides with the alkali metals [12], while, as we established, in certain cases, these fluorides are not completely soluble in an acid medium and can contaminate the precipitate of quadrivalent uranium.

During oxidimetric titration with vanadate, contamination of the uranium precipitate with trivalent vanadium cannot be allowed, since it is oxidized by the vanadate to the quadrivalent state: ($V^{III} + V^{V} \rightarrow 2V^{IV}$).

A solution was found in the difference in solubility of the double fluorides of vanadium (III) and uranium (IV); the

TABLE 2

Determination of Uranium in the Presence of Vanadium (20 mg), Molybdenum (15 mg), and Titanium (15 mg) by Reduction with Divalent Iron in 1 N Sulfuric Acid, Containing 2% Sodium Sulfate and 10% (by Volume) of Hydrofluoric Acid

0.01 N U solution taken, ml	0.01 N NH_4VO_3 used, ml	Deviation		U found in the filtrate, mg
		0.01 N solution, ml	U mg	
8,72	8,38	—0,34	—0,40	0,11
8,72	8,47	—0,25	—0,29	0,11
9,13	8,86	—0,27	—0,32	0,09
9,13	8,81	—0,32	—0,38	0,11
22,89	22,50	—0,39	—0,46	0,13
22,89	22,60	—0,29	—0,34	0,15
22,89	22,50	—0,39	—0,46	0,12
				0,12
	Mean	—0,32	—0,37	

TABLE 3

Determination of Uranium in the Presence of Iron (350 mg), Vanadium (20 mg), Molybdenum (15 mg), and Titanium (15 mg) by Reduction with Divalent Iron in 1 N Sulfuric Acid, Containing 2% Sodium Sulfate and 10% (by Volume) of Hydrofluoric Acid

0.01 N U solution taken, ml	0.01 N NH_4VO_3 used, ml	Deviation	
		0.01 N NH_4VO_3 used, ml	U, mg
7,57	7,35	—0,22	—0,26
7.57	7,23	—0,34	—0,40
7,57	7,31	—0,26	—0,31
12,70	12,52	—0,18	—0,21
12,70	12,34	—0,36	—0,42
12,70	12,39	—0,31	—0,36
12,70	12,42	—0,28	—0,33
12,70	12,44	—0,26	—0,30
12,70	12,52	—0,18	—0,21
12,70	12,42	—0,28	—0,33
	Mean	—0,27	—0,31

fluoride Na_2VF_5 is considerably more soluble and remains in solution in 1 N sulfuric acid, while the fluoride $NaUF_5$ is precipitated quantitatively. For this purpose, it is essential that the concentration of the sodium salt should not exceed 2%.

The effect of other foreign elements was eliminated, mainly in two ways. Some of these elements are removed from the sphere of reaction in that they stay in solution during precipitation of uranium (IV) fluoride, these elements include, e.g., niobium, tantalum, molybdenum*, titanium, and other elements whose fluorides

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*Under the conditions used for reducing uranium, molybdenum is reduced to molybdenum blue which remains in solution as a colloidal suspension, so that, in practice, it is possible to remove it almost completely by washing it off the precipitate.

TABLE 4

Comparative Results for the Determination of Uranium by the Fluoride and the Hydrosulfite Method [5] in Control Samples

Sample No.	Impurities in the aliquot, in mg				U found (%) by the following methods:		Deviation, relative, %
	Fe^{III}	V^{V}	Mo^{VI}	Ti^{IV}	fluoride	hydro-sulfite	
1	None	None	None	None	53,17	52,80	+0,7
1	—	—	—	—	52,83	—	+0,0
1	—	—	—	—	53,31	—	+1,0
1	350	20	15	15	53,37	—	+1,1
1	350	20	15	15	53,22	—	+0,9
1	350	20	15	15	53,11	—	+0,6
1	350	20	15	15	53,11	—	+0,6
P-X	None	None	None	None	1 ,37	14,94	+2,8
P-X	»	»	»	»	15,22	—	+1,9
P-X	350	20	15	15	15,23	—	+1,9
P-X	350	20	15	15	15,26	—	+2,1
Cl-X	None	None	None	None	10,56	10,45	+1,0
Cl-X	»	»	»	»	10,61	—	+1,4
Cl-X	350	20	15	15	10,60	—	+1,4
Cl-X	350	20	15	15	10,59	—	+1,3
VII-b	None	None	None	None	3,06	3,13	−2,2
VII-b	»	»	»	»	3,14	—	+0,3
VII-b	»	20	15	15	3,12	—	−0,3
VII-b	»	20	15	15	3,12	—	−0,3

are soluble in an acid medium. Another part of the elements is precipitated partially with uranium fluoride (IV), but do not interfere further during the oxidimetric determination of uranium, these elements include, e.g., iron (III)*, aluminum**, calcium**, and the rare earths**.

Tables 2 and 3 contain results for the determination of uranium in synthetic mixtures, containing appreciable amounts of trivalent iron, vanadium, molybdenum, and titanium.

As already indicated above, all the results are characterized by a deviation of 0.3-0.35 mg of uranium on the low side. This deviation is composed of two factors: the solubility of $NaUF_5$ during its precipitation in 1 N sulfuric acid, and during washing of the precipitate. These losses were compensated by a) using an empirical titer for the vanadate, the latter was established by using a standard solution of sexivalent uranium, and titrating the precipitate of $NaUF_5$ which was isolated and washed under the conditions used in the experimental procedure, or b) by applying a correction of 0.30-0.35 mg of U. Table 4 contains comparative results for the determination of uranium by two methods in two samples with different uranium contents, and also containing iron, vanadium, molybdenum, and titanium.

Experimental Procedure for the Determination of 3-60% of Uranium in the Presence of Iron, Vanadium, Molybdenum, and Titanium

Depending on the expected content of uranium, an aliquot of 0.2 to 1 g of sample is decomposed as usual by boiling in a mixture of nitric acid (sp. gr. 1.4) and hydrochloric acid (sp. gr. 1.19) and excess acid removed by evaporation. To the residue is added 23-25 ml of sulfuric acid and the mixture heated to the appearance of thick white fumes. 50-60 ml of water is added and the whole boiled for 20-30 minutes to dissolve the salts. Solution plus precipitate is transferred to a 200 ml standard flask. The solution obtained contains approximately 2 N sulfuric acid.

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*Before titration with vanadate, the washed precipitate of the fluorides is treated with sulfuric acid in the presence of boric acid, during which the double fluoride of trivalent iron $Na_3[FeF_6]$ is decomposed, and the iron (III) oxidizes the uranium to form the equivalent amount of ferrous iron which is then oxidized by vanadate.

**Appreciable amounts of calcium, aluminum, and the rare earths may exhibit interference. The method of removing such interference is described in the experimental procedure.

In order to determine uranium, 25.00-50.00 ml* of this solution is pipetted into a platinum basin or a paraffin beaker** and the necessary reagents added in such amounts that the final volume of 100 ml contains the following: 1 N sulfuric acid, 2% Mohr's salt, 2% anhydrous sulfate, and 10% (by volume) of 40-48% hydrofluoric acid. The solution is thoroughly mixed until the salts have completely dissolved and then it is left to stand for 5 hours or overnight. The precipitate is filtered through a paraffined funnel using a fine filter paper (blue band), and the filtrate collected in a paraffined beaker. The precipitate is transferred onto the filter paper and washed with wash liquor with a pH of about 2 (50 ml of hydrofluoric acid + 40 g ammonium acetate + distilled water to 1 liter) until the wash liquors give a negative reaction for divalent iron (test with 5-orthophenanthroline, α,α'-dipyridyl*** or permanganate).

Depending on the expected concentration of uranium, the determination is completed by titration with 0.01 or 0.005 N ammonium vanadate. For this purpose, the washed precipitate together with the filter paper are transferred to a 250-300 ml conical flask which contains 90 ml of a 33% by volume acid, 10 ml of saturated solution of boric acid, and 2-3 drops of a 0.1% solution of phenylanthranilic acid. The solution is thoroughly mixed and then titrated with vanadate to the appearance of a rosy violet color which becomes more intense with time.

Determination of uranium in 10-12 samples takes 10-12 hours, not taking into account the time for which the precipitate is allowed to stand.

SUMMARY

A titrimetric method has been developed for the determination of uranium in the presence of iron, vanadium, molybdenum, and titanium; it is based on the fact that divalent iron in sulfuric acid, in the presence of hydrofluoric acid, reduces uranium (VI), and the quadrivalent uranium is precipitated in the form of the double fluoride $NaUF_5$; the uranium determination is finished vanadometrically.

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*The aliquot chosen should be such that 10-20 ml of a 0.01 or 0.005 N solution of oxidizing agent is used for titration. In the presence of large amounts of calcium, or the rare earths, care should be taken that the aliquot does not contain more than 25-30 mg of Al_2O_3, or more than 20-25 mg of calcium or total rare earths, since large precipitates complicate washing somewhat, and can lead to high results at the expense of divalent iron.
**Since plexiglass apparatus is not readily available at the moment, and the analysis is carried out at room temperature after decomposing the sample, vessels which have been covered with paraffin can be used (200-300 ml beakers, funnels). The vessels are recoated with paraffin as the need arises.
***Orthophenanthroline or α,α'- dipyridyl are used as follows for testing that the precipitate has been washed completely: the funnel is filled with wash liquor which is then collected in a platinum basin, a few crystals of α,α'-dipyridyl or phenanthroline are added to the basin and the crystals and liquid mixed by swirling the basin. In the absence of ferrous ions the solution remains colorless; when ferrous ions are present the solution acquires a rose color.

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QUANTITATIVE DETERMINATION OF OXYGEN
IN THE LOWER OXIDES OF TITANIUM
BY MEANS OF X-RAY ANALYSIS

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Under the conditions of gradual oxidation of titanium, solid solutions are formed by the penetration of oxygen atoms into the octahedral cavities of the crystal lattice of α-Ti. According to Ehrlich [1] solid solutions of oxygen in α-titanium are formed up to the composition $TiO_{0.42}$. All the phases with a variable composition $Ti_{0\to 0.42}$ can be called the lower oxides of titanium. The conditions for the formation of the lower oxides of titanium, and also of its other oxides with a higher oxygen content are being studied fairly thoroughly at present. The equilibrium phase diagram for the system titanium–oxygen [2] is known.

Radiographical studies of the lower oxides of titanium [1, 2] have shown that the curve relating the lattice constant c and the oxygen content of the α-titanium, which possesses a hexagonal crystal lattice, is steep. This makes it possible to attempt to use a radiographic method for the quantitative determination of oxygen dissolved in α-titanium. Such an attempt was made in the work described here.

Synthesis of the Preparations of the Lower Oxides of Titanium. In order to check on, and get more accurate values than the published ones, we prepared and examined radiographically some preparations of the lower oxides of titanium TiO_x from $TiO_{0.05}$ to $TiO_{0.60}$ through $x = 0.05$. Titanium iodide in the form of small bars was used as the original material. The purity of the titanium was 99.8%, while the impurities present and their amounts were 0.05% Si, 0.05% Mg, 0.03% Fe, 0.01% Cu and 0.06% others.

In contrast to previous workers [1, 2] who prepared the lower oxides of titanium by sintering titanium metal with TiO_2, we synthesized preparations by saturating powdered titanium with gaseous oxygen. Titanium in the form of a fine powder which readily reacts with gaseous oxygen, was prepared by the hydride method. The oxygen and hydrogen contents of the titanium power thus prepared were determined by a vacuum extraction method [3]. Analysis showed that the oxygen concentration was 0.04% by weight, while the hydrogen content was 0.003% by weight.

A quartz boat filled with titanium powder (about 1.5 g) was placed in a quartz tube and the air pumped out of the system; the temperature was gradually taken up to 350° until all the gases and traces of moisture adsorbed by the powder had been removed by continuous operation of an oil diffusion pump. The calculated amount of oxygen, obtained by the electrolysis of water, was then allowed into the cooled system. The oxygen pressure in a known volume was measured by a mercury U-shaped manometer. In the temperature range 500-550° complete absorption of the oxygen by titanium was observed. The amount of absorbed oxygen was also determined from the gain in weight of the sample. Preparations of the titanium oxides obtained in the form of powders were pressed in columns into the form of cylinders at a pressure of about 8000 kilogram/cm^2, and kept for 15 hours at a temperature of 1000 ± 20° in a quartz tube in order to achieve a uniform distribution of oxygen in the preparation.

Weighing of the calcined samples of the oxides from $Ti_{0.05}$ and $Ti_{0.30}$ showed that their weight decreased by 0.4-0.7 thousandths part of a gram as the result of the evaporation of the lower oxides of titanium, since a small bluish film was observed on the inner walls of the tube [1].

The preparations of the lower oxides of titanium obtained, on fracture, have a light grey color, and on being triturated become dark.

Samples of $TiO_{0.20}$ and $TiO_{0.40}$ were analyzed for oxygen and hydrogen by the vacuum fusion method [3]

Calculated O_2 content % wt.	O_2 found by the vacuum method, %
6.40	6.37
11.77	11.75

The calculated amount of oxygen absorbed by the sample was taken as a basis.

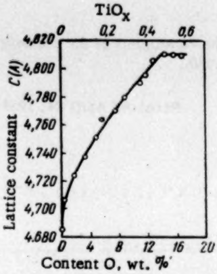
Radiographical Determination of Lattice Constants. The preparations of the lower oxides of titanium obtained, after being ground into a fine powder, were annealed in a vacuum at 500-600° for 30 minutes in order to relax the stress of the crystal lattice, they were then examined radiographically by the powder method (Debye-Scherrer). It was essential to get the most accurate values of the lattic constants of the test samples. This could be carried out either by using the x-ray method of "reciprocal photography" in a camera of type 1 KROS, or by the asymmetric method of Straumanis and Jevins [4]. We used the latter method since it ensures that clearer radiograms are obtained in the region of large scattering angles for shorter exposures than is possible when the method of "reciprocal photography" is used. The technical details of the asymmetric method for the precision determination of the lattice constants of the elementary cell of crystals have been described previously [5]. One of the most important conditions for ensuring the maximum accuracy of the method is the preparation of very fine powder samples, with a thickness of less than 0.2 mm, prepared by depositing on filaments of borlithium glass a fine layer of the test powder by means of non-drying flexible dope.

Composition and Values of the Lattice Constants for the Lower Oxides of Titanium

Chemical composition			*a* (*A*)	*c* (*A*)	*c*/*a*
TiO_x	O, *aT* %	O wt., %			
α-Ti	0	0	2,9510	4,6850	1,5875
$TiO_{0,012}$	1,19	0,40	2,9515	4,7054	1,5942
$TiO_{0,053}$	5,03	1,74	2,9556	4,7225	1,5978
$TiO_{0,102}$	9,27	3,30	2,9610	4,7370	1,5998
$TiO_{0,154}$	13,24	4,87	2,9640	4,7510	1,6029
$TiO_{0,193}$	16,20	6,05	2,9670	4,7616	1,6049
$TiO_{0,248}$	19,62	7,62	2,9695	4,7701	1,6064
$TiO_{0,299}$	22,95	9,06	2,9703	4,7789	1,6089
$TiO_{0,337}$	25,06	11,10	2,9702	4,7901	1,6127
$TiO_{0,401}$	26,55	11,77	2,9685	4,7950	1,6153
$TiO_{0,451}$	31,01	13,03	2,9705	4,7992	1,6156
$TiO_{0,513}$	33,87	14,60	2,9710	4,8105	1,6192
$TiO_{0,510}$	35,82	15,71	2,9704	4,8101	1,6193
$TiO_{0,600}$	37,53	16,68	2,9701	4,8097	1,6194

In order to remove the fluorescent background which develops during x-ray analysis of titanium-containing materials, we used a second x-ray plate placed between the sample and the main plate as a screen. The radiograms obtained in this way had a considerably weakened background, and contained all the weak lines; under these conditions, the K_α lines with large angles were clearly duplicated.

Radiograms were taken in ordinary cameras with a diameter of 57.3 with copper radiation, the operating conditions of the tube being 35 kilovolts and 14 milliamps. The exposure on an average was 12 hours. In order to calculate the lattice constants a and c, bright, readily duplicated lines with the indices (2133) and (3032), and having angles of the order of 69 and 73° respectively were chosen. The lines were measured on the radiograms in an IZA-2 comparator with an accuracy of ± 0.01-0.02 mm. The values of the lattice constants calculated from these two lines had an accuracy of ± 0.0004 A. A check on the value of the constant c, carried out for several samples on the basis of the line (0006) showed that the results agreed. We used the following



The relation between the lattice constant c and the oxygen content in the lower oxides of titanium: c = f (x).

values of the wavelengths for the calculations: $\lambda CuK\alpha_1$ = 1.54050 A and $\lambda CuK\alpha_2$ = 1.54434 A. The final values of the lattice constants were calculated as the arithmetic mean of four possible combinations for the lines: $21\bar{3}3\alpha_1$, $21\bar{3}3\alpha_2$, $30\bar{3}2\alpha_1$ and $30\bar{3}2\alpha_2$.

The composition of the preparations of the lower oxides of titanium which we studied and the values of their lattice constants are given in the table. Titanium oxide which we prepared and which contained 0.40% by wt. of oxygen, according to our analysis, was used as the preparation with a composition of $TiO_{0.012}$

Indexing of the radiograms showed that all the lines observed for samples ranging from the original titanium to an oxide with a composition of $TiO_{0.5}$ belong to the hexagonally closely packed structure α Ti. Starting with the oxide $TiO_{0.5}$ on the radiograms there appeared a system of weak lines corresponding to the phase on a variable composition based on TiO. Thus, it can be assumed that the homogeneity boundary of solid solutions of oxygen in α-Ti corresponds approximately to the composition $TiO_{0.48}$.

The Standard Curve c = f (x) for Determination of Oxygen. As is evident from the Table, the lattice constant c changes to a considerably greater extent than the constant a in the lower oxides of titanium, with increasing oxygen content. For solving our problem therefore we used the values of the constant c.

On the basis of the tabulated results, a curve was constructed relating the lattice constant c to the oxygen content of the lower oxides of titanium [i.e., the curve c = f(x)] The oxygen content in wt. % was plotted along the abscissa, as well as the values of the oxygen coefficient x in the formula TiO_x. This curve can be used as a standard for the quantitative determination of oxygen in the lower oxides of titanium belonging to the binary system titanium—oxygen. By maintaining the accuracy which we achieved for the determination of the lattice constant c, which is equal to ± 0.0004 A, the accuracy of determining oxygen by means of the curve c = f x) by the interpolation method amounts to ± 0.1% wt. of oxygen on an average. In the region of very low oxygen contents (at approximately up to 1% wt. of oxygen) the accuracy will be even higher. As is evident from the curve, the maximum solubility of oxygen in α-Ti corresponds approximately to 14.4% wt. In order to determine oxygen quantitatively in the lower oxides of titanium by the x-ray method, radiograms are taken of the test material in the form of a powder, the lattice constant c being measured with the maximum accuracy. The value found for c is plotted on the curve c = f (x) in the form of a circle with a radius with corresponding accuracy in A. The oxygen content corresponding to this point is read off the abscissa and the accuracy evaluated. A determination takes 15-18 hours when the x-ray tube is operated under ordinary conditions.

SUMMARY

Preparations of the lower oxides of titanium have been synthesized containing from 0 to 17% wt of oxygen. It has been found that the homogeneity region of the lower oxides of titanium extends up to a composition corresponding to $TiO_{0.48}$ (14.4% wt. oxygen).

The relationship between the lattice constant c and the oxygen content of the lower oxides has been used for the quantitative determination of oxygen in the lower oxides of titanium by a radiographic method, with an accuracy of ± 0.1% wt.

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THE POLAROGRAPHY OF THE NOBLE METALS (A REVIEW)

N. K. Pshenitsyn, N. A. Ezerskaya, and M. B. Bardin

The first successes in the field of the polarographic determination of the noble metals have mainly been achieved in the course of the last few years. The use of a dropping mercury electrode is connected with some difficulties which are specific for the noble metals. A large number of the complex compounds of the noble metals are reduced by metallic mercury, and this chemical interaction does not permit their polarographic determination. In the case of the other complex compounds, the main obstacle to their electrical reduction within the potential limits used in polarography as their high stability. The platinum metals (with the exception of palladium) possess the capacity to depress the hydrogen overvoltage on mercury, and this leads to the development of catalytic hydrogen waves which mask the waves which arise as the result of the reduction of the platinum metal, or which complicate their interpretation.

The difficulties indicated have been overcome mainly by adopting one of the following approaches:

a) choosing a reagent which forms a complex compound with the noble metal, which is not reduced by mercury and gives a diffusion current in a potential region more positive than the reduction potential of the supporting electrolyte;

b) by using the catalytic current of hydrogen which, in certain cases, is proportional to the concentration of the platinum metal;

c) by replacing the dropping mercury electrode by an electrode made from a more noble metal, e.g., platinum.

Towards the end of 1957 the oscillographic comparative titration method was suggested for the determination of some of the platinum metals [1].

Each of the approaches just mentioned has its advantages and disadvantages; accordingly, in choosing the method to be adopted, each particular case must be judged separately on its own merit.

The present article is a brief review of the work carried out on the polarography and amperometry of the noble metals, which has been published up to the end of 1958.

The half-wave potentials of the noble metals in various supporting electrolytes, and schemes for the electrode processes, for a large part of the work published up to the end of 1955, have already been incorporated in A Table of the Half-Wave Potentials of Inorganic Depolarizers" compiled by Vlcek [2].

Gold. Hrman [3] during a study of the behavior on a dropping electrode of the complex compounds formed during the interaction of $HAuCl_4$ with excess Na_2SO_4, Na_2HPO_4, $NaHCO_3$, KSCN, KCN, and KOH established that only $KAu(OH)_4$, $KAu(CN)_4$, $KAu(CN)(OH)$ and $KAu(CN)_2$ are sufficiently stable to reduction by metallic mercury. For analytical purposes he suggested the use of potassium hydroxocyanoaurate, and recommended his technique for the determination of gold in ores. A subsequent check on this method [4-6] showed that this method is not suitable for the determination of small amounts of gold, and that it is better to use the complex hydroxy compounds of trivalent gold. Polarographic determination of gold in the form $KAu(OH)_4$ in the presence of gelatin, has been recommended for the determination of gold in silver [4, 5], in industrial cyanide solutions, sludge, and assay beads [6-7] and in ruby glass [8].

A group of Czech workers have confirmed the possibility of determining gold in the form of complex hydroxy compounds [9]. Of special interest is the possibility which they established of polarographing gold from solutions of ethylenediamine [10], ethyelenediamine tartrate [11], and a combination of the latter with complexons [12], or with sodium pyrophosphate [13]. A mixture of ethylenediamine tartrate and sodium pyrophosphate [13] has made it possible to develop a method for the selective polarographic determination of gold, in which only metals which are reduced at more positive potentials (Hg, Ag, and Pt) interfere. In all probability this method will be used for the analysis of gold-containing materials with a large content of impurities (alloys, concentrates, sludges, etc.).

Gutman and Schober [14] while carrying out a polarographic study in anhydrous ethylenediamine containing $NaNO_3$ as the supporting electrolyte, obtained a wave for the reverse reduction of Au (III). The current is proportional to concentration over the range 10^{-1} to 10^{-3} M.

A number of authors have shown that it is possible to obtain polarographic waves for gold on a stationary platinum electrode [15-16], and on a rotating microelectrode [17]. In the case of the latter, the diffusion current which corresponds to the reduction of Au(III) to the metal, is proportional to the gold concentration from 1×10^{-5} to 3×10^{-3} M.

Platinum. Herasymenko and Slendyk [18], and Slendyk [19] have suggested a method for the polarographic determination of traces of platinum in palladium on the basis of the catalytic hydrogen wave, the height of which is approximately proportional to the platinum concentration in solution. The most satisfactory results were obtained at a concentration of 2 M with respect to HCl, and at a platinum concentration from 10^{-6} to 10^{-7} M.

The choice of a complex compound of platinum which would be suitable for its polarographic determination on a dropping electrode has proved very difficult. It has been found that it is impossible to get polarographic waves for the complex chlorides and bromides of di- and quadrivalent platinum [20]; and for cyanides of Pt^{II} [20-21]; complexes with ammonia, ethylenediamine [21]; and pyridine [21-22]. Subsequently, however, Rius an and Molera [23] obtained clearly defined polarographic waves during the reduction of the complex cyanides of quadrivalent platinum.

English [24] has developed a method for the polarographic determination of platinum in an organic catalyst using as a supporting electrolyte a mixture of citric acid and sodium hydrophosphate (pH 7). Under such conditions, a reduction wave for Na_2PtCl_6, which has a somewhat unusual shape, starting at zero applied emf and finishing around -0.6 volt (saturated calomel electrode) is obtained. The wave height is measured at a point corresponding to -0.3 volt. The experimental accuracy is 0.2% for a platinum content of 3.5 mg in 50 ml of solution.

Laitinen and Onstott [25] have shown that the ion $[PtCl_4]^{2-}$ is adsorbed on the electrode and is thereafter reduced on the electrode at low emf values.

Scarano [26] obtained a wave for H_2PtCl_6 in a supporting electrolyte of saturated NaCl, with three diffusion regions. The height of the first, and also the total height of the second and third waves was found to be linearly related to the platinum concentration.

Simpson, Evans, and Saroff [27] have established that it is possible to get a wave for quadrivalent platinum in a supporting electrolyte of an acetate buffer solution. Values of the diffusion coefficients for noble metal ions as calculated by means of the Ilkovich equation are included in their paper.

Of interest is a study of the behavior of certain complex compounds of quadrivalent platinum, including those with: hexamine and triethylenediamine [28], the halogeno- and hydroxy pentamines [29], and also the tetramines of divalent platinum [30], and compounds containing 1, 10-phenanthroline [31]. In a supporting electrolyte of KCl and KNO_3, and also in KNO_3 in the presence of NH_4OH, platinum (IV), in solutions of the first two compounds, is reduced to the divalent state, while at potentials more negative than -1.3 volt (saturated calomel electrode) it is reduced to the metal. Clearly defined waves are obtained, in which the diffusion current is proportional to the platinum concentration. The hydroxy- and chlorpentamine complexes of platinum behave in similar fashion. On replacing the molecule of NH_3 in $[Pt(NH_3)_6]^{4+}$ by a halogen there is observed a shift in $E_{1/2}$ to more negative values. A study of the ions of platinum tetramine has shown that the trans-isomer is reduced more readily than the cis-isomer.

Beran and Dolezal [32] using a supporting electrolyte consisting of a mixture of ethylenediamine tartrate and thiocyanate, obtained a reduction wave for $[Pt(en)(CNS)_2]$ the height of which was proportional to the platinum concentration within the limits 4×10^{-5} to 3×10^{-3} M. Chlorides, nitrates, sulfates, and Complexon III do not interfere. Fe^{3+} forms a precipitate which adsorbs the platinum. Cu, Te, Ce, Pd, and Au complicate the determination. The experimental error is ± 4%. The drawback of the method is the long time taken to form the ethylenediaminethiocyanate of divalent platinum (12 hours).

Bardin and Lyalikov [33-34] were the first to show that it is possible to use solid platinum electrodes for the determination of platinum. In a supporting electrolyte of 0.1 N $NaNO_3$, platinum, in the form of H_2PtCl_6, is reduced to the metal at + 0.3 volt (saturated calomel electrode). The diffusion current is proportional to the platinum concentration. The experimental accuracy is + 7%. The effect of foreign ions has not yet been studied.

Palladium. Willis [21] has studied in detail the polarographic behavior of complex compounds of palladium with potassium cyanide, ammonia, pyridine, and ethylenediamine. Within a certain concentration range (not more than 5×10^{-3} M), the author obtained clearly defined waves which can be used for analytical purposes. The author has pointed out that with increasing basic properties of the amine, $E_{1/2}$ becomes more negative, while the reduction becomes less reversible.

Rius and Molera [23] in contradicting the results of Willis, have noted that palladium is not reduced on a dropping electrode from a solution of cyanide.

Wilson and Daniels [35] having studied the conditions for the polarographic determination of palladium in an ammoniacal supporting electrolyte (i.e., in the form $[Pd(NH_3)_4]^{2+}$, established that platinum and appreciable amounts of rhodium, iridium, and gold affect the diffusion current of palladium and have recommended that palladium be precipitated beforehand with dimethylglyoxime.

Simpson, Evans, and Saroff [27] obtained a clearly defined wave for palladium starting at an applied emf of 0 volt on using a supporting electrolyte of acetate buffer and 0.06 M HCl.

Depending on the acetate and chloride concentrations, the diffusion coefficient of the $[PdCl_4]^{2-}$ ions was found to vary within the limits $0.4\text{-}0.8 \times 10^{-5}$ cm^2 sec^{-1}.

Linhart [36] has suggested a method for the polarographic determination of palladium in the presence of gold and platinum in a supporting electrolyte of lithium hydroxide. The method permits palladium to be determined in alloys with gold ("white gold") with an accuracy of ± 1%, and also palladium and gold in an alloy with platinum.

Tomicek and co-workers [9-10] have investigated the possibility of determining palladium polarographically in a supporting electrolyte of hydroxides and various amines. Ethylenediamine tartrate was found to be a particularly valuable supporting electrolyte, this permits determination of gold and palladium in each others presence. The use of ethylenediamine tartrate in conjunction with various complexons [11-13] permitted a method to be developed for the determination of palladium in the presence of Pb^{2+}, Cd^{2+}, As^{3+}, Sb^{3+}, Sn^{2+}, WO_4^{2-}, MoO_4^{2-}, Fe^{3+}, Zn^{2+}, Sn^{4+}, Cr^{3+}, Co^{2+}, Mn^{2+}, and U_2^{2+}; Cu^{2+} and Bi^{2+} interfere.

Bardin and Lyalikov [37] have shown that it is possible to determine palladium polarographically by using platinum stationary and rotating electrodes. Under certain conditions, the waves obtained can be used for analytical purposes. The experimental accuracy is about ± 3% for palladium concentration limits of 5×10^{-5} to 2×10^{-2} M.

Iridium. Numerous attempts to obtain current—voltage curves for iridium on a dropping mercury electrode have not met with success, since most of the complex compounds of quadrivalent iridium, on coming into contact with mercury, are reduced to trivalent iridium compounds; the latter are not usually reduced at potentials preceding the reduction potential of the supporting electrolyte. Accordingly, Willis [21] who tried out complex compounds of iridium with potassium cyanide, potassium thiocyanate, ammonia, pyridine, and ethylenediamine for polarographic purposes, and Repin [22] who tried sodium chloride, sodium phosphate, Seignette salt, and tetraethylammonium iodide as supporting electrolytes for the polarographic determination of iridium (III), were unsuccessful. The polarographic curves of iridium (IV) in a supporting electrolyte of sodium chloride and gelatin, which West, Dean, and Breda obtained [38], were so nebulous in form that the authors themselves did not study them any further. Recently, Pshenitsyn, Ezerskaya, and Ratnikova [39] obtained curves for the reduction of the chloroiridate ion, and oxidation curves for the chloroiridite ion, on a rotating platinum electrode. The diffusion current of iridium (IV) corresponding to its reduction to the trivalent state, is proportional to the iridium concentration, and permits the latter to be determined within the limits 2×10^{-3} to 5×10^{-6} M. iridium. The experimental accuracy is ± 5%. Rhodium, platinum, palladium and several non-noble metals do not interfere with iridium determination.

Rhodium. Willis [40] who has studied in detail the reduction of a large number of the complex compounds of Rh (III) on a dropping mercury electrode, found that some of them $[Rh(CN)_6]^{3-}$, $[Rh(NH_3)_5Cl]^{2+}$, $[Rh(CNS)_6]^{3-}$ and $[RhPy_6]^{3+}$ form clearly defined polarographic waves whose height is proportional to the rhodium concentration of the solution. The author is of the opinion that the best of these compounds for quantitative determination is $[RhPy_6]Cl_3$.

Repin [22] has also used the pyridine compound of rhodium (III) for determination of rhodium, but attributed another composition to the complex $[RhPy_5Cl]Cl_2$. Iridium in any amount, and platinum in equal amounts to rhodium, do not interfere with the determination of rhodium in a pyridine supporting electrolyte (more than 0.001 g/ liter). An oscillographic method for the determination of rhodium suggested by Beran and Dolezal [41] has proved very promising. In a supporting electrolyte of 0.1 M HCl + 0.6 M NaCl, in the presence of rhodium there is formed a characteristic sharp peak in the anodic part of the curve. The peak height is linearly related to the rhodium concentration (from 0.5 to 25 γ of rhodium in 20 ml solution). The method described can be used for the determination of rhodium in the presence of 2000-3000 times its amount of platinum, palladium, and gold with reasonable accuracy.

Quite a few papers have been published on the study of the polarographic behavior of rhodium. However, the complex fluorides [38], chlorides and nitrates [42] studied are insufficiently stable with respect to mercury, and are, apparently, not very suitable for analytical purposes. The biscyclopentadienyl of trivalent rhodium $[Rh(C_6H_5)]X_2$ [43] is reduced on the dropping electrode; nevertheless, because of the difficulty of preparing it, it does not seem to have much promise for analytical use.

Ruthenium. It has been established by Willis [21] that it is impossible to reduce on a dropping mercury electrode the solutions of the complex cyanides, thiocyanate, and ammines (NH_3 and Py) of tri- and quadrivalent ruthenium, because of the stability of these compounds. On the other hand, the complex chloride of Ru (IV) is reduced on coming into contact with mercury. In order to find reduction waves for ruthenium, Niedrach and Tevebaugh [44] chose a non-complex compound—ruthenium perchlorate (IV). In a supporting electrolyte of 0.1-5 N $HClO_4$, they obtained three well shaped curves, one of which can be used for the quantitative determination of ruthenium, as long as conditions can be found for converting the ruthenium quantitatively into the perchlorate. Recently, Brancia, and Mesaric [45] obtained in a supporting electrolyte of oxalic, tartaric, and citric acids, reduction waves for ruthenium which are proportional to the ruthenium concentration within the limits 4 to 120 γ/ml. Unfortunately, the authors have not established the valence of the ruthenium before and after reduction, nor the character of the ruthenium compound with the hydroxy acids. Silverman and Levy [46] who studied the oxidation and reduction of compounds of sexi, septi-, and octivalent ruthenium K_2RuO_4, $KRuO_4$, and RuO_4 (in a supporting electrolyte of $NaClO_4$), and also De Ford and Davidson [47] who studied the oxidation of the complex cyanides of di- and trivalent ruthenium, used a platinum electrode instead of a dropping mercury electrode, and obtained well shaped current—voltage curves. The authors of these articles, who were not carrying out this work for analytical purposes, nevertheless pointed out [46] that there is a proportionality between the current and the ruthenium concentration within the limits 6×10^{-4} to 1.2×10^{-3} M. Further checking and study of the reduction conditions, probably could lead to the use of some of these electrode reeactions for the quantitative determination of ruthenium. However, neither the ruthenate or the perruthenate, because of their instability, nor the cyanides because of the difficulty of preparing them, can be regarded as compounds which are suitable for the determination of ruthenium within the general scheme of the analysis of the platinum metals. This is true to an even greater extent to the determination of ruthenium (on a dropping mercury electrode) in the form of ruthenocene $Ru(C_5H_5)$ and its salts which give reduction and oxidation waves a in a supporting electrolyte of $NaClO_4$ [48]. Since, according to the observations of Heyrasymenko and Slendyk [49], the catalytic waves of hydrogen formed in the presence of ruthenium are particularly large, they can be used for the determination of very small amounts of ruthenium. El Guebely [50] who measured the hydrogen catalytic wave in solutions of $Ru_2(SO_4)_3$ in 0.01 N H_2SO_4 and 0.1 N Na_2SO_4, determined the extremely small amounts of ruthenium of 2×10^{-7} - 5×10^{-10} mole/liter. The linear relation between the current and the concentration is preserved in the concentration range indicated with an accuracy of 5-10%, but breaks down on increasing the ruthenium concentration. Susic [51] determined ruthenium on the basis of the catalytic currents which develop in the presence of a mixture of tri- and quadrivalent ruthenium in a solution of 0.9 M $HClO_4$, in a solution of 0.1 M Complexon II (pH > 5) or 0.05 M Complexon II and 0.5 M ammonium acetate. The author recommends the first supporting electrolyte for the determination of from 0.01 to 0.37 γ/ml of Ru, and the second and third for the determination of more than 0.1 γ Ru/ml. It should be pointed out that Susic's results do not agree with the results of Niedrach and Tevebaugh [44], who obtained reduction waves for tri and quadrivalent ruthenium in a supporting electrolyte of $HClO_4$, but no catalytic waves for hydrogen.

Osmium. Crowell, Heyrovsky, and Engelkemeir [52] were the first to study the reduction of osmium on a dropping electrode. These authors established that it is impossible to determine osmium tetroxide or its compounds in acid solutions polarographically because of their interaction with metallic mercury. Polarographic determination is only possible in alkaline solutions; the best results were obtained by these authors in a supporting electrolyte of saturated solutions of $Ca(OH)_2$ and $Ba(OH)_2$. The polarograms thereby obtained have three diffusion regions corresponding to the successive reduction of Os (VIII) to Os (VI), Os (IV), and Os (III), and can be used for the quantitative determination of osmium at concentrations of the latter of the order of 10^{-4} M. Subsequently, these results were confirmed by Meites [53] coulomometrically. Meites also studied in detail the reduction of osmium (VIII) in a supporting electrolyte of mineral (phosphoric, sulfuric, hydrochloric, and perchloric acids) and organic (tartaric and citric) acids, in some buffer solutions, in an ammoniacal solution of ammonium chloride, and in potassium cyanide and potassium thiocyanate. In the author's opinion, osmium is best determined polarographically in cyanide solutions. Rius and Molera [23] had previously obtained reduction waves for Os (VI) in a supporting electrolyte of KCN.

Kolthoff and Parry [54] used for the polarographic determination of osmium the catalytic wave for the decomposition of hydrogen peroxide which develops as the result of the following reactions:

$$\mathrm{Os(VIII)} + 2e \rightarrow \mathrm{Os(VI)} \quad \mathrm{Os(VI)} + 2H^+ + H_2O_2 \rightarrow \mathrm{Os(VIII)} + 2H_2O$$

The wave height, which depends on both the osmium concentration and the hydrogen peroxide concentration, is measured according to the current which arises at a potential of +0.23 volt with respect to the saturated calomel electrode.

Amperometric Titration

a) Using a Dropping Mercury Electrode. Kolthoff and Langer [55] have used α-nitroso-β-naphthol for titrating palladium. The titration was carried out in an acetate buffer solution at a potential of -0.6 volt (saturated colomel electrode), under which conditions both palladium and the reagent give diffusion currents.

Tomicek and co-workers [56] established that it is possible to titrate palladium amperometrically with dimethylglyoxime, salicylaldoxime, 8-hydroxyquinoline, and mercaptobenzothiazole. Best results were obtained with dimethylglyoxime. Titration was carried out in a short circuited system (at 0 volt applied emf) in a supporting electrolyte of an acetate buffer solution or 0.1 N HCl, 0.05 N HNO_3, and 0.1 N KNO_3. The experimental accuracy is about 2%. Large amounts of gold interfere; Ag^+, Cd^{2+}, Zn^{2+}, Pb^{2+}, Bi^{3+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Al^{3+} etc. do not interfere.

Wilson and Wilson [57] have recommended 1, 2, 3-benzotriazole for titrating palladium. Pt, Rh, Ir and a number of nonnoble metals do not interfere with titration by this reagent. Os, Ru, Au, Fe, and Ni interfere. The experimental accuracy for determination of palladium is ± 0.3%.

Milenko and Susic [58] have titrated gold (III) in H_2SO_4 solution at 0 volt by means of ascorbic acid.

b) Using a Rotating Platinum Electrode. Ezerskaya [6] has suggested a method for titrating gold (at 0 volt applied emf) using sodium thiosulfate or mercaptobenzthiazole. The first reagent permits determination of gold at a concentration of the order of 10^{-5}, while the second permits determination of 10^{-6} mole/liter with completely satisfactory accuracy. Iron and large amounts of copper interfere. Interference from iron can be suppressed by adding KHF_2.

Reishakhrit and Sukhobokova [59] have developed a method for the determination of gold in the presence of palladium, selenium, and tellurium by titration with hydroquinone. The titration was carried out at a potential of +1.0 volt in a supporting electrolyte of 2 N H_2SO_4 at 60°. The end point was established on the basis of the increasing wave for the oxidation of hydroquinone. For gold contents of 10^{-2} to 10^{-4} mole/liter, the experimental accuracy varies from 1 to 10%.

Bardin and Lyalikov [60] have shown that palladium can be titrated amperometrically with α-furildioxime, while Bardin and Melika [61] have shown that β-furfuraldoxime can be used. For palladium contents ranging from 10^{-4} to 10^{-2} mole/liter, titration can be carried out with an accuracy of 2-3%.

Pshenitsyn and Ezerskaya [62] have suggested a method for the amperometic titration of iridium with hydroquinone or ascorbic acid, for iridium contents ranging from 0.002 to 1.0 mg of iridium per ml. Only gold and large amounts of ruthenium and iron interfere with the titration of iridium under the conditions chosen.

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A RAPID MICROMETHOD FOR THE DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS

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The problem which confronted us was to search for a simple micromethod for determining halogens, both in monomers and polymers, which would require simple apparatus and would be suitable for compounds containing other elements in addition to halogens.

Many microanalytical methods are known for the determination of halogens in organic compounds; catalytic oxidation by combustion of test material in an oxygen stream using a platinum catalyst [1]; the Carius method [2]; fusion of the test material with potassium metal [3]; combustion of the organic material in a stream of oxygen, the halogen being trapped by silver metal [4] with simultaneous determination of carbon, hydrogen, and halogen. All these methods require fairly complicated apparatus, and, with the exception of the last method, it is necessary to transfer the test halogen into another vessel.

Of interest is the rapid micro method of determining halogens suggested by Schoniger [5] which is carried out in a simple apparatus. Combustion of the organic test material is carried out in a flask filled with oxygen, the halogen liberated being then titrated in the same flask.

Combustion of a material in vessels filled with oxygen was first suggested in 1892 by Hempel [6] for the macrodetermination of sulfur in coal and other organic materials; the method was subsequently improved in coal and other organic materials; the method was subsequently improved by Graefe [7] and Marcusson and Doscher [8]. The latter determined halogens also by this method. This method, however, did not find wide application since combustion was carried out in flasks of too large a volume amounting to 6-10 liters, which often cracked. In 1922 Votocek [9-11] developed this method further and used it for the determination of chlorine in organic materials. Later, Mikl and Pech [12, 13] determined halogens and sulfur, both independently, and in each other presence, in organic materials.

All the variants mentioned above for the determination of halogens and sulfur by combustion in a vessel filled with oxygen were used for macroaliquots of 0.5-0.1 g. Schoniger [5], for the microdetermination of halogens, cut down the weight of sample to 4-8 mg and the capacity of the flask to 300 ml. Chlorine and bromine were determined acidimetrically by Viebock's method [14] using mercury cyanate.

For halogen determination we modified the construction of the flask, since the flasks used by Schoniger have some essential drawbacks. We used conical or flat bottomed flasks with a side arm and a tap for connecting to the atmosphere. The ground glass stopper had a drawn out end so that it was possible to fuse a platinum wire* into it.

Chlorine and bromine were determined by titrating with mercuric nitrate or perchlorate, while iodine was determined as the iodate by Leipert's method [15] using sodium thiosulfate as titrant.

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*A flask without a side arm (as used by Schoniger) is not suitable to work with. It is sometimes impossible to remove the stopper on account of the vacuum which develops in the flask after absorption of the combustion products. The use of a stopper with a drawn out end, as in our construction, makes it easy to fuse the platinum wire into it without damaging the stopper.

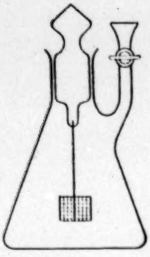


Fig. 1

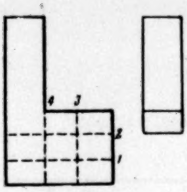


Fig. 2

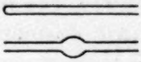


Fig. 3

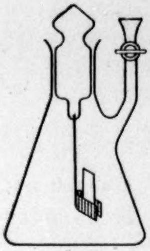


Fig. 4

An aliquot of the halogen-containing organic material is wrapped up in ashless filter paper and the latter fastened to the platinum wire fused into the drawn out end of the stopper; the latter is rapidly ignited in the flask filled with oxygen. The halogen thereupon is quantitatively converted to the hydrogen halide which is absorbed by a solution of alkali. The halogen is titrated in the same flask.

Apparatus. Determination is carried out in a conical or flat bottom flask made of heat-resistant glass, and with a capacity of 200-350 ml; the flask is fitted with a ground glass stopper and is provided with a side arm. The latter is provided with a tap and terminates in a funnel (Fig. 1). The bottom of the stopper is drawn out, and into the drawn out end is fused a platinum wire 70-80 mm long and 0.7-0.8 mm in diameter, depending on the height of the flask used. The platinum wire should not get closer than 20-30 mm to the bottom of the flask. To the end of the wire is fastened a platinum grid 20× 30 mm in size; the grid is attached to the wire either by bending the latter or by welding it on.

Ashless filter paper made by the D. I. Mendeleev Moscow Chemico-Technological Institute was used for combustion of the test materials; the shape and size of the filter papers are shown in Fig. 2. For analysis of liquids, capillary tubes with a small expanded portion in the middle, or without such an expanded portion, were used, the latter being fused at one end (Fig. 3).

Experimental Procedure. An aliquot of solid test material (3-15 mg, in certain cases up to 50 mg depending on the halogen content), is weighed out by difference from a weighing tube onto the center of the filter paper; the latter is then carefully wrapped up by folding along the dotted lines (Fig. 2).

Nonvolatile liquids are taken in capillaries. It is useful to seal one end of such capillaries with a small piece of paraffin wax, since the latter helps complete conversion of the halogen into the hydrogen halide and also prevents loss.

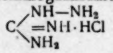
The capillary plus test material are also wrapped up in filter paper in such a way that the open end of the capillary is covered by several layers of paper.

The sample is wrapped up in the filter paper as if it were a little parcel . The parcel is fitted into the platinum grid, so that the long narrow end of the filter paper is pointing upwards (Fig. 4). The lower part of the platinum grid is bent upwards slightly so that the sample is held securely in position and its complete combustion is ensured.

Determination of Chlorine and Bromine. 10 ml of distilled water, 1 ml of 2 N potassium hydroxide, and 3 drops of hydrogen peroxide are placed in the flask for absorbing the halogen. In order to expel the air from the flask, oxygen is passed into it from a cylinder, through a flask containing 50% potassium hydroxide, for 2-3 minutes at the rate of 100-120 ml per minute. The upper end of the filter paper is then ignited and the stopper rapidly inserted in the flask. During the combustion process, which lasts 15-20 seconds, the flask should be left at rest, the stopper must, however, be firmly kept in position by hand in order to prevent the gases formed from forcing it out.

When combustion is complete, in order to accelerate absorption of the combustion products, the flask is vigorously shaken for 6-10 minutes until the cloud over the liquid in the flask has disappeared completely.

TABLE 1

Test material	Sample weight, mg	Chlorine content, %		Deviation, %
		found	theoretical value	
Lead triphenylchloride	4,025	7,50	7,50	±0
$(C_6H_5)_3$ PbCl	5,200	7,29		−0,21
Dithoxylylchorohydrinxylithane	5,345	7,67	7,69	−0,02
$C_{19}H_{21}S_2O_7Cl$	4,805	7,79		+0,10
Lead diphenydichloride	4,045	16,07	16,40	−0,33
$(C_6H_6)_2PbCl_2$	4,375	16,27		−0,13
Sodium p-chlorobenzene sulfonate	3,920	16,23	16,52	−0,29
	5,640	16,30		−0,22
$C_6H_4ClSO_3Na$				
Dinitrochlorobenzene	4,550	17,38	17,50	−0,12
$C_6H_5Cl(NO_2)_2$	24,365	17,31		−0,19
p-Chlorophenylmethacrylamide	3,050	18,33	18,12	+0,11
$ClC_6H_4NHCOC_3H_5$	4,620	18,38		+0,16
p-Nitrobenzylchloride	4,390	20,97	20,66	+0,31
$C_6H_4CH_2NO_2Cl$	4,860	20,90		+0,24
p-Thiocyanochlorobenzene	5,640	21,17	20,90	+0,27
C_6H_4ClCNS	5,275	21,09		+0,19
	3,560	20,90		±0
Aminoxylithane hydrochloride		21,11	20,91	+0,20
$C_5H_{12}O_3NCl$		21,21		+0,30
p-Chloronitrobenzene	2,785	22,59	22,52	+0,06
$C_6H_4NO_2Cl$	4,265	22,69		+0,16
p,p'-Aminochlorodiphenyl	5,380	17,55	17,39	+0,16
$(C_6H_4)_2NH_2Cl$	4,705	17,20		−0,19
Chlorbenzoic acid	7,640	22,87	22,64	+0,23
ClC_6H_4COOH	6,095	22,93		+0,29
p-Chlorphenol	3,365	27,66	27,62	+0,04
$C_6H_4(OH)Cl$	3,940	27,78		+0,16
p-Chloroaniline	3,950	27,59	27,93	−0,34
$ClC_6H_4NH_2$	3,670	27,58		−0,35
Semicarbazide hydrochloride	4,280	31,84	31,78	+0,06
$H_2NCONHNH_2HCl$	5,055	31,80		+0,02
Aminoguanidine hydrochloride	3,675	32,14	32,07	+0,07
 $C\left\langle\begin{matrix}NH-NH_2\\=NH\cdot HCl\\NH_2\end{matrix}\right.$	3,540	32,18		+0,11
2,3-Dichloro-4,5-dimethylstyrene	3,410	35,05	35,28	−0,23
$C_6H_4(CH_3)_2Cl$	3,580	34,94		−0,34
2,4,6-Trichlorophenylmetacrylamide	2,645	40,42	40,22	+0,20
$Cl_3C_6H_2NHCoC_3H_5$	4,000	40,19		−0,03
Tetrachlorophthalic acid	2,925	45,42	45,37	+0,05
$C_6Cl_4(COOH)_2{}^1/_2H_2O$	3,450	45,33		−0,04
Tetrachlorophthalic anhydride	4,065	49,28	49,25	+0,03
$C_6Cl_4C_2O_3$	3,300	49,63		+0,38
2,4,5-Trichlorotoluene	4,540	54,34	54,41	−0,07
$Cl_3C_6H_2CH_3$	2,930	54,13		−0,28
Hexachlorobenzene	3,845	74,47	74,70	−0,23
C_6Cl_6	3,260	74,54		−0,16

Unless the flask is shaken, absorption of the combustion products may take 45-60 minutes. Before opening the flask, a small amount of distilled water is poured into the side arm and into the throat surrounding the stopper. The vacuum in the flask is destroyed by opening the tap in the side arm, the stopper is then easily lifted out. The stopper and platinum wire plus grid are carefully washed with distilled water over the flask.

TABLE 2

Test material	Sample weight, mg	Chlorine content found, %		
		in a flask filled with O_2	in O_2 current	by fusion with potassium
Copolymer of isoprene and chloro-styrene, Sample IVS* No. 13	5,290	13,42	—	—
	4,440	—	13,44	—
The same No. 25	2,910	24,55	—	—
	34,590	—	—	24,21
The same No. 32	5,670	11,05	—	
	7,860	—	10,98	
The same No. 34	3,515	11,12	—	—
	3,020	11,10	—	—
	5,460	—	10,96	—
The same No. 35	5,425	17,51	—	—
	5,060	17,82	—	—
	6,285	—	17,82	—
The same No. 39	5,490	22,82	—	—
	5,295	22,93	—	—
	3,245	—	22,63	—
	4,455	—	22,92	—
Three-dimensional polymer Mark KFUKh, Sample* No. 25	4,400	9,45	—	—
	4,520	9,57	—	—
	27,845	—	—	9,25
The same No. 1	2,685	10,61	—	—
	26,670	—	—	10,61
The same No. 2	4,140	10,80	—	—
	3,115	10,93	—	—
	36,940	—	—	11,19
The same No. 4	4,225	10,50	—	—
	5,060	—	10,73	—
Polychlorovinyl	4,450	56,35	—	—
	3,470	56,43	—	—
	3,115	—	56,42	—
	3,305	—	56,23	—
Chloride residue in treated chitin	39,960	0,23	—	—
	51,310	0,18	—	—
	35,435	—	—	0,28
	28,290	—	—	0,22
The same No. 32	40,010	0,33	—	—
	44,730	0,34	—	—

*A sample prepared in the Institute of High Polymer Compounds.

In order to decompose the hydrogen peroxide, the flask is boiled for 5 minutes, the solution is then cooled and acidified with 0.5 N nitric acid to a pH of 2.3-2.5*. The total volume of liquid in the flask before titration is 20-25 ml. Titration is carried out in the same flask as that used for the combustion; titration is carried out with 0.01 N mercuric perchlorate** or nitrate in the presence of 2-3 drops of a 1% solution of diphenylcarbazone to the appearance of a weak rose color.

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*The amount of nitric acid taken is sufficient to neutralize the alkali completely and to leave 0.5 ml of acid in excess. For new solutions of alkali and acid, the amount of nitric acid required for neutralizing the alkali to the phenolphthalein endpoint is determined anew.

**0.01 N $Hg(ClO_4)_2$ is prepared by dissolving, on heating, 1.1 g of HgO in 4 ml of 30% $HClO_4$. The solution is diluted with 50 ml of water and filtered, the filter is carefully washed and the volume made up to 1 liter with distilled water.

TABLE 3

Test material	Sample weight, mg	Bromine content, %		Deviation, %
		found	theoretical	
Methylbromophthalimide	5,000	33,24	33,21	+0.03
$BrCH_3C_6H_2O_2NH$	4,435	33,03		−0,18
Dimethylbromostyrene	2,745	37,81	37,91	−0,10
$(CH_3)_2BrC_6H_2CH=CH_2$	2,550	37,62		−0,29
p-Bromonitrobenzene	3,500	39,58	39,55	+0.03
$BrC_6H_4NO_2$	4,545	39,48		−0,07
p-Bromobenzoic acid	3,085	39,81	39,72	+0.09
BrC_6H_4COOH	3,305	39,54		−0,18
2,3,3-Trimethylpentene-1-bromo-6	2,660	41,88	41,91	−0.03
$C_8H_{15}Br$	2,840	42,00		+0.09
5,7-Dibromo-8-hydroxyquinoline	2,895	52,80	52,75	+0.05
$Br_2C_9H_4(OH)N$	3,610	52,74		−0,01
p-Dibromobenzene	5,605	67,45	67,74	−0.29
$C_6H_4Br_2$	5,110	67,63		−0,11

TABLE 4

Test material	Sample weight, mg	Iodine content, %		Deviation, %
		found	theoretical	
Sample No. 281	4,775	25,75	25,67	+0.08
$C_{22}H_{27}ON_2SI$	4,050	25,46		−0,21
Sample No.366	3,745	26,22	26,24	−0,02
$C_{21}H_{29}ON_2SI$	3,015	26,43		+0.19
Sample No. 207	2,190	27,25	27,13	+0,12
$C_{20}H_{25}ON_2SI$	3,315	26,89		−0,24
α-(Nitrofurylpropyl) methylquinoline iodide	4,380	29,95	29,92	+0.03
	4,140	29,90		−0,02
$C_{17}H_{17}NNO_2OI$				
Iodoalkylate-1-methyl 2 (p-tolyl)	3,780	34,61	34,85	−0,24
benzimidazol	3,690	34,61		−0,24
$C_{16}H_{17}N_2I$				
m-Iodobenzoic acid	3,460	52,27	51,39	−0,12
IC_6H_4COOH	4,090	51,24		−0,15
β-Iodopropionic acid	9,250	63,40	63,47	−0,07
ICH_2CH_2COOH				

Determination of Iodine. For the determination of iodine, the liquid used for absorption is 10 ml of distilled water with 1 ml of 2 N potassium hydroxide, no hydrogen peroxide being added as in the case of chlorine and bromine. Combustion is carried out as in the case of determination of chlorine and bromine. Iodine is determined by the Leipert method [15]—by oxidation of iodine to iodate, with subsequent titration of iodate with 0.02 N sodium thiosulfate, using starch as indicator.

It is necessary to carry out blank determinations with the solutions used in the actual determination (by combustion of filter without any sample) of the halogens. Results of the experiments described are given in Tables 1-4. One determination of a halogen using one flask takes 25 minutes. When four flasks are used, four determinations can be carried out in 1 hour. A shaker is recommended for shaking the flasks.

SUMMARY

The possibility has been demonstrated of introducing into the practice of organic microanalysis a rapid method for the determination of halogens (chlorine, bromine, and iodine) using sample weights of 3 to 15 mg; for low halogen contents the sample weight can be increased to 50 mg. The experimental accuracy is ± 0.3%.

The method consists of the combustion of test material, wrapped up in filter paper, in a flask filled with oxygen; the combustion products are absorbed with an alkali solution, and the halide is then determined titrimetrically in the same flask. The method can be used for both low molecular weight compounds and high molecular weight compounds which are difficult to burn. The presence of sulfur, of nitrogen in any form whatever, and of lead does not interfere with the determination. The method is distinguished by the simplicity of the apparatus used, and by the speed with which it can be carried out; it can be recommended for serial mass analysis.

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QUANTITATIVE DETERMINATION OF CH_2-GROUPS IN OPEN CHAINS CONTAINING NOT LESS THAN FOUR LINKS

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Determination of the individual components of more or less high molecular weight fractions of petroleum is impossible because of the astronomical number of possible isomers. The characteristicsof such mixtures can be given in the form of the relative content of various functional groups from which the molecules of the material studied can be constructed. For this purpose calculations are based on the average molecule of the fraction.

The methane-naphthenic part of the hydrocarbons of petroleum or bitumen can be characterized by the method of infrared spectroscopy in parts of the content of CH_3 and CH_2-groups. These groups are determined separately, mainly on the basis of the vibrations of the CH bond. Both the valence and the deformation CH-vibrations for CH_3 and CH_2-groups have different frequencies and are characterized by differences in the absorption intensity. The present article touches on the use of the deformation vibrations of the CH-bond for the quantitative determination of the content of CH_2-groups forming open chains with not less than four links (CH_2).

The deformation vibrations of the CH-bond in methylene groups appear in the region 800-700 cm^{-1} in the form of a wide absorption band. Normal paraffins in the liquid state give a single band at 720 cm^{-1}. In the case of crystalline, normal paraffins, liquid acids, and other compounds containing methylene chains, the band splits into two components [1, 2, 3].

The position of the absorption maximum depends [4] on the number of CH_2-groups in a continuous chain (Table 1).

Thus, molecules not containing chains of CH_2 groups with a number of CH_2 groups of four and more, do not give any absorption at 13.8-13.9 μ (725-720 cm^{-1}). Hastings and Anderson in 1951 suggested a method for the quantitative determination of all CH_2 groups in open chains by means of the integral absorption in the region 12.5-14.3 μ. This idea was used by Francis for the analysis of high molecular weight compounds [5]. The existence of a quantitative connection between the molecular absorption coefficient for this band and the number of CH_2-groups in the molecule has been pointed out in the collection of articles by West [6]. In order to carry out calculations on the basis of the method suggested for all the absorption region, obviously, one value should be a adopted for the group absorption coefficient.

However, actual results confirming this latter hypothesis are not available; its arbitrary nature is obvious.

We have made an attempt to investigate separately, from the point of view of quantitative determination, the absorption in the region 13.2-14.4 μ, i.e., to limit ourselves to determination of only CH_2-groups forming continuous chains containing not less than four links.

The work was carried out on a single beam apparatus IKS-11. The spectra were registered for a layer of 0.05 mm of the pure individual materials without using a solvent.

The area of the absorption band was measured on the curves relating optical density to wavelength, constructed by conversion. This area was that outlined by the optical density curve within the limits 13.3-14.4 μ and the "base line" produced as a tangent to the inflection points of the optical density curve. In Fig. 1 is shown the shape of the band, the recording of the apparatus, and the area measured.

TABLE 1

The Relation between the Characteristic Frequencies of the Deformation Vibrations of CH_2 Groups and Chain Length [4]

No. of CH_2 groups in the chain	Position of the absorption maximum (μ)
1	12.7-13.0
2	13.2-13.5
3	13.74
4	13.80
5	13.83
6	13.85
More than 6	13.86

The area was measured by means of transparent squared paper [7]. Calculation of the CH_2-groups content can be calculated in terms of one mole or 100 g of material. In order to show that the area S found is a measure of the CH_2-groups in a molecule, it is necessary to show that the value S/n is a constant (n is the number of CH_2-groups in a molecule). Bearing in mind that the measurements were carried out for one layer thickness for all materials, i.e., with a different number of molecules, it was necessary to refer the results obtained to an equal number of molecules in the layer. The number of molecules in the layer should be inversely proportional to the molar volume (the ratio of the molecular weight to the density of the M/d material can be arbitrarily taken as the molar volume. Thus the constant should have the value SV_M/n [8].

The results obtained are given in Table 2. The average group coefficient makes it possible to find the number of CH_2-groups contained in the average molecule of a fraction, as long as the molecular weight and the density are known; the number of CH_2-groups is the quotient obtained by dividing SV_M by this coefficient (equal to 204 in our case).

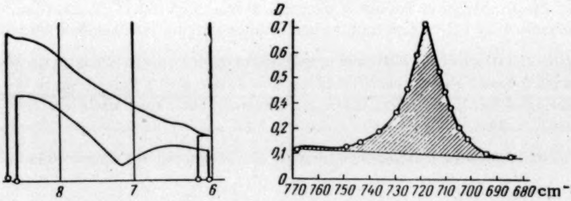

Figure. Dodecane, layer 0.05 mm; on the left—apparatus recorder chart with index lines [6, 7, 8], lined ready for calculation; on the right—optical density curve obtained by conversion.

The group absorption coefficient for solid materials differs appreciably from the coefficients for liquids; the calculated constant SV_M/n has a different value in the case of solid materials, the constancy of this value has not yet been established. The examples at our disposal are given in Table 3. Some authors are of the opinion that studies should only be carried out for the liquid phase, the solid materials being studied in the molten state. This position is rather indefinite since the absorption intensity should also depend directly on the temperature.

Calculation of the weight content of CH_2-groups in a given material is shown in Table 4. The constant calculating coefficient in this case will be

$$K = \frac{S}{cdx}$$

where c is the weight concentration of CH_2-groups (%); d is the specific gravity; and x is the layer thickness.

TABLE 2

Measurement of the Integral Absorption Intensity in the Region 13.2-14 μ for Calculation of the Number of CH_2-Groups in a Molecule

Test material	S, cm²	V_M	n	$\frac{SV_M}{n}$	$\Delta\frac{SV_M}{n}$	$\frac{\Delta n}{n}\cdot 100$
Heptane	7,35	149	5	219	+15	7,4
Octane	6,96	162,5	6	189	−15	6,3
Nonane	7,5	179	7	192	−12	6,0
Decane	7,7	195	8	188	−16	8,0
Undecane	9,35	212	9	221	+17	8,0
Dodecane	9,1	227	10	206	+ 2	1,8
Tridecane	9,25	244	11	205	+ 1	0,05
Pentadecane	9,30	276	13	197	− 7	0,35
Hexadecane	10,45	293	14	218	+14	0,70
Heptadecane	9,82	311	15	204	0	0
				$\frac{SV_M}{n}=204$	±10	3,8

TABLE 3

Measurement of the Integral Absorption Intensity in the Region 13.2-14 μ for Solid Materials

Test material	S	V_M	n	$\frac{SV_M}{n}$
$C_{36}H_{74}$	8.55	649	34	163
$C_{20}H_{42}$	8.0	364	18	162
Stearic acid $C_{17}H_{35}COOH$	7.85	336	16	164

In order to obtain the percentage weight content of CH_2-groups in an unknown material, it is necessary to divide S by Kdx, i.e., by 14.55 d (for a layer of 0.05 mm).

The results given in Tables 2 and 4 show that the mean error varies within the limits 0-8%, both for calculation of the number of groups in a molecule, and of the content by weight. The error amounts to ± one group for the determination of the number of groups. Experimental accuracy can be increased by more accurate measurement of the area, by careful purification of the standard materials and by increasing the number of individual materials examined. Thus, the methylene groups of paraffin chains can be determined quantitatively. The methylene groups of the naphthenic rings do not exhibit absorption in the given spectral region.

In order to evaluate the possibility of using the method considered in practice, synthetic mixtures of liquid methane and methane-naphthene hydrocarbons were made, and analyzed for their content of CH_2-groups (Table 5). In order to carry out calculations for mixtures, it is necessary to assume that the properties of the components making up the mixture are additive, and this can lead to some error. The specific gravity and the molecular weight assumed for calculating the concentration of CH_2-groups in mixtures were obtained as mean values on the basis of the assumption of additivity. The mixtures were prepared on a weight basis from the small number of individual materials at our disposal. The total amount of a mixture did not exceed 0.5-0.7 g.

The inconvenience, for purpose of calculation, of using the values of M and d, which in many cases, cannot be determined, is completely eliminated by studying the materials in solution. In this case the calculation is carried out on the basis of the appropriate conversion constant, established by carrying out measurements of

TABLE 4

Measurement of the Integral Intensity in the Region 13.2-14.4 μ for Calculation of the Percentage Weight Content of CH_2-Groups

Test material	s	c	d	$K=\frac{S}{cdx}$	$c=S/Kdx$	$\Delta c/c\cdot 100$
Heptane	7,35	70	0,684	3.08	74,1	5,9
Octane	6,96	63,7	0,703	2,69	68,0	7,7
Nonane	7,50	76,6	0,718	2,73	71,7	6,7
Decane	7,70	78.9	0,730	2,67	72.9	7,6
Undecane	9,35	80,8	0,741	3,12	86,2	6,7
Dodecane	9,1	82,5	0,751	2,94	83,0	0,6
Tridecane	9,25	83,7	0,757	2,92	83,7	0
Pentadecane	9,30	84,9	0,770	2,84	83,1	2,12
Hexadecane	10,45	85,9	0,774	3,14	92,5	7,7
Heptadecane	9,82	86,7	0,775	2,94	87,1	0,46
	Mean value			$K=2,91$	—	4,6

TABLE 5

Analysis of Synthetic Mixtures of Hydrocarbons for Their CH_2-group Content ($n \geq 4$)

Components of the mixture	Wt. ratio	d, mean	Molecular ratio 1 : 2	M, mean	V_{measured}	S	No. of CH_2-groups in a molecule		Percentage wt. cont., CH_2-groups	
							taken	found	ethylcyclohexane	decane
Ethylcyclohexane Decane	1,335	0,765	1,69	124	162	3,02	2,97	2,4	33,8	26,8
Cyclohexane Dodecane	0,243	0,756	0.49	143	191	7,52	6,71	6,86	66,4	67,5
The same	1,780	0,772	3,60	103	131	3,33	2,18	2,14	29,6	29,2
Isooctane Dodecane	1,282	0,720	1,92	133	187	3,54	3,42	3,2	36,0	34,1
Ethylcyclohexane Dodecane Isooctane	1,767 4,230 1,000	0,748	1,73 2,74 0,96	144	192	6,07	5,06	5,71	49,9	55,8

the absorption of individual materials in solution. The number of the given groups in a liter of solution is determined directly; after this it is possible to convert into percentage by weight of groups, or number of groups in the material. Unfortunately, it is difficult to find an appropriate solvent for determination of CH_2-groups at 720 cm^{-1}; only carbon disulfide which does not absorb in this region might be suitable, and, possible, polyfluoroethylene. The absence of a solvent prevented us from carrying out this most interesting part of the work.

SUMMARY

It has been shown that it is possible to carry out a quantitative determination of long chain CH_2-groups by measuring the integral absorption in the region 13.3-14 μ.

A preliminary determination of the group adsorption coefficient is necessary, since it has different values for different apparatus and experimental conditions.

When liquid and solid substances are studied, it is necessary to know the molecular weight and density of the substances studied in order to calculate the CH-group content in the number of groups in a molecule, whereas in order to calculate the percentage weight content of CH_2-groups, it is only necessary to know the density. The value of the density is not required for the determination of the percentage weight content of CH_2-groups in solution.

The experimental accuracy was found to be ± 1 group for the calculation of the number of groups per molecule, and about 10% for the calculation of the percentage weight content of the groups.

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BRIEF COMMUNICATIONS

LITHIUM TETRA-(p-TOLYL) BORON AS A REAGENT FOR THE QUANTITATIVE DETERMINATION OF SODIUM

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In recent years several articles have appeared which have been devoted to the tetraarylboron salts $MeBAr_4$, where Me is the cation of an alkali metal, while Ar is an aromatic or heterocyclic radical. The interest displayed in these compounds is determined mainly by their capacity to precipitate certain cations in aqueous solutions. Thus, sodium tetraphenyl boron precipitates the cations K^+, Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+ etc. There are more than one hundred papers devoted to the use of sodium tetraphenylboron in analytical chemistry. However, among known salts of this type there are no sodium salts which are sparingly soluble in water, and in which form sodium could be determined quantitatively. According to available results [1], the solubility of $MeBAr_4$ salts in water depends on the nature of the aryl radical in the anion.

Having used a reaction described previously [2] of a magnesium organic compound with sodium borofluoride, we found that during the interaction of p-tolylmagnesium bromide with $NaBF_4$ sodium tetra(p-tolyl) boron which is sparingly soluble in water is formed:

$$NaBF_4 + n = CH_3C_6H_4MgBr \rightarrow NaB(C_6H_4CH_3)_4.$$

Lithium tetra-(p-tolyl) boron, a salt which is readily soluble in water, is obtained from sodium tetra-(p-tolyl) boron by a double exchange reaction with $LiBF_4$ in alcoholic solution:

$$NaB(C_6H_4CH_3)_4 + LiBF_4 \rightarrow LiB(C_6H_4CH_3)_4 + \downarrow NaBF_4.$$

lithium tetra-(p-tolyl) boron forms colorless crystals which are readily soluble in water, alcohol, acetone, and ether; it is insoluble in petroleum ether. An aqueous solution of the lithium salt gradually changes in contact with air. Lithium tetra (p-tolyl) boron in aqueous solutions precipitates Na^+, K^+, Rb^+, Cs^+, etc.

Wittig and Herwig [3] synthesized lithium tetra (p-tolyl) boron from tri (p-tolyl) boron and p-tolyl lithium; the authors do not point out that this salt precipitates sodium ions.

We have used lithium tetra (p-tolyl) boron for the quantitative determination of sodium. A 10-13% solution of lithium tetra (p-tolyl) boron (1.85-2.0 g) in water was prepared; to this was added 2-3 drops of a 3% solution of NaCl before formation of a precipitate, in order to saturate the solution beforehand with sodium tetra (p-tolyl) boron. The solution was then filtered. The reagent prepared in this way was used for sodium determination. To 1 ml of an aqueous solution of NaCl containing 0.0301 g of NaCl was added 3-4 ml of reagent; after 5-10 minutes, the precipitate was transferred to a crucible fitted with a filter, and the rest of the precipitate washed onto the filter crucible by means of reagent solution. The precipitate was washed 4-5 times with 1.5-2 ml lots of reagent solution, after which it was dried at room temperature in a desiccator (under a small vacuum) over P_2O_5. The dry precipitate was then washed free from $LiB(C_6H_4CH_3)_4$ by means of anhydrous ether; it was finally dried in a desiccator (at room temperature) to constant weight.

The experimental results obtained by this method are given in the Table.

Amount of NaCl per ml, g	Weight of $NaB(C_6H_4CH_3)_4$ precipitate		Sodium content of the NaCl, %	
	found	calculated	found	calculated
0.0301	0.2044	0.2052	39.18	39.34
0.0301	0.2050	0.2052	39.30	39.34
0.0301	0.2047	0.2052	39.23	39.34
0.0454	0.3085	0.3094	39.22	39.34

The fact that lithium tetra (p-tolyl) boron precipitates not only Na^+, but also K^+, Rb^+, and Cs^+ will not interfere with its use for determining sodium, since all these cations, apart from sodium, can be quantitatively precipitated beforehand with lithium tetraphenylboron.

An advantage of the method suggested is that it is possible to carry out the work with only small amounts of the tetra (p-tolyl) boron salts, since the sodium tetra (p-tolyl) boron obtained during the analyses is readily reconverted by double decomposition with $LiBF_4$ into $LiB(C_6H_5CH_3)_4$, which can be used for subsequent analyses. Moreover, by using lithium tetra (p-tolyl) boron, it is possible to determine sodium in the presence of lithium, a determination which cannot be carried out by means of the method with uranyl acetate and zinc, since Li^+ forms a sparingly soluble ternary salt with the latter.

Lithium tetra (p-tolyl) boron should not be kept long in air; accordingly, it is best to prepare it immediately prior to use.

Synthesis of Sodium Tetra (p-tolyl) Boron. To 3.5 g of finely ground $NaBF_4$ in a small volume of absolute ether is added a still warm solution of Grignard reagent prepared from 20 g of p-bromotoluene and 2.8 g of magnesium in 70 ml of anhydrous ether (the reaction is carried out in a flask provided with a stirrer and a reflux condenser). The reaction mixture is heated on a water bath for 1.5 hours; after cooling, it is filtered through a No. 1 glass filter. The precipitate on the filter is washed 3-4 times with anhydrous ether. To the ether filtrate consisting of unreacted Grignard reagent is added another 3.5 g of sodium borofluoride, and all the operations repeated. Both precipitates are combined and treated with a small amount of water to remove sodium borofluoride. Sodium tetra (p-tolyl) boron is filtered on a No. 2 glass filter and washed three times with water; it is dried at room temperature in a vacuum desiccator over P_2O_5, for complete removal of moisture. If the precipitate treated with water is kept for a long time on the filter, and air sucked through it, or it is kept in a damp state for a long time in air, then it decomposes. The dried material is dissolved in the minimum amount of acetone. The solution is filtered and absolute ether added to it until no further precipitate is formed. The sodium tetra (p-tolyl) boron is filtered, and washed several times with absolute ether. The yield of the salt is 1.2-1.7 g (10-13% in terms of the p-bromotoluene used).

Found %: C 84.01, 83.89, H 7.29; 7.10; Na 5.99, 5.85 $C_{28}H_{28}BNa$: Calculated %: C 84.41; H 7.09; Na 5.77.

Sodium tetra (p-tolyl) boron in a pure, dry state is fairly stable; it is readily soluble in acetone and ethyl acetate; soluble in alcohol and pyridine; sparingly soluble in water, and insoluble in benzene and absolute water; it is sparingly soluble in wet ether.

The Synthesis of Lithium Tetra (p-Tolyl) Boron. To a solution of 2.5 g of sodium tetra (p-tolyl) boron in the minimum amount of absolute alcohol is added an alcoholic solution of 1.2 g of lithium borofluoride. The precipitate of sodium borofluoride formed is filtered off. The alcohol is removed in a vacuum desiccator over $CaCl_2$. The dry residue is dissolved in absolute ether and filtered free from the undissolved sodium borofluoride taken in excess, and the unreacted sodium tetra (p-tolyl) boron. The ether is removed in a vacuum desiccator. The dry residue is transferred onto a No. 3 or No. 4 glass filter and washed four times with low boiling petroleum ether to free it from ditolyl impurities. Residual petroleum ether is removed in a vacuum desiccator. 2.2 g of lithium tetra (p-tolyl) boron is obtained (85% of theory). This salt is readily soluble in acetone, alcohol, ether, and water; it is insoluble in petroleum ether. Lithium tetra (p-tolyl) boron in the solid state and in solution does not keep under ordinary conditions; the salt content of its solutions decreases with time; after several hours standing in air, an aqueous solution of $LiB(C_6H_4CH_3)_4$ will no longer give a precipitate with a solution of NaCl.

Analysis of lithium tetra (p-tolyl) boron with the object of determining its lithium content is carried out as follows: an aliquot of the salt is decomposed with 0.1 N HCl. After some time, excess acid is back titrated with alkali.

Found % Li 7.82. $C_{28}H_{28}BLi$: Calculated %: Li 1.81.

The lithium tetra (p-tolyl) boron formed in this way, on dissolving it in water, gives slightly turbid solutions; the solution is carefully filtered before using it for determining sodium.

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THE EXACT DEFINITION OF PEAK POTENTIAL IN OSCILLOGRAPHIC POLAROGRAPHY

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Analysis of solutions by the method of oscillographic polarography reduces to measurement of the potential and the peak height of the diffusion current. The peak potential depends on the nature of the ion studied, while the height is proportional to its concentration. However, in addition to the electrochemical reactions which take place on the electrode, charging of the electrical double layer occurs. The current which corresponds to this process is proportional to the rate of change of potential and reaches a considerable value. The presence in the electrolysis cell of several substances which participate in the electrochemical reaction, also complicates determination by the method of oscillographic polarography. Usually, to the diffusion current (i_d) of the test ion are added other currents (i_b), so that the total current in the electrolysis cell circuit is determined by their sum [1, 2]:

$$i = i_d + i_b. \tag{1}$$

At the point where the diffusion current passes through its maximum, $di_d/dE = 0$ (E is the electrode potential). Differentiation of (1) at the peak gives

$$di/dE = di_b/dE. \tag{2}$$

Accordingly, the method which has been in use previously (Fig. 1a) for measurement, in which the peak potentials of the total and diffusion current are identified with each other, should be replaced by a more refined method, the principle of which is shown in Fig. 1b. Here the peak potential is defined as the point at which the curves for the total current and for the supporting electrolyte have the same slope. If this technique is not adopted then

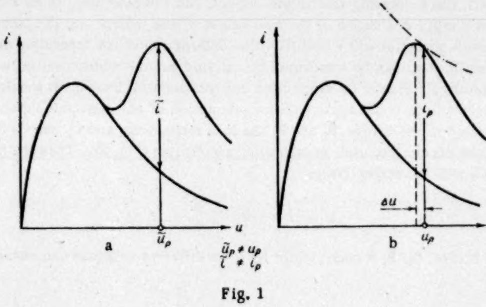

Fig. 1

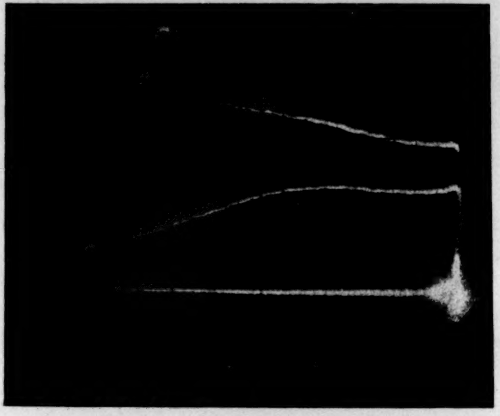

Fig. 2. 20 γ Cd^{2+}/ml in 1 M KCl, α 8.5 volt/second, t = 25°. Dropping mercury electrode, anode polarization with pre-electrolysis.

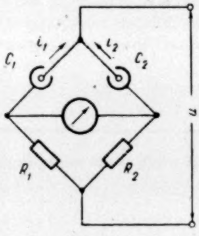

Fig. 3.

there will be an error not only in the value of the potential of the maximum, but also in the value of the current which will not be a maximum. The error in the value of the potential is often greater than 10 millivolts in practice, while the rate of change of potential a and the concentration C of the ion participating in the electrochemical reaction will affect its value. The capacity current which makes up part of i_b increases in proportion to a. The curvature of the peak increases with concentration C. Accordingly, the error increases on increasing α and decreasing C. This explains the potential shift on changing the concentration. While the ohmic drop in potential, on increasing the concentration, always shifts the peak towards the higher voltage applied to the cell, the direction of the shift caused by the supporting electrolyte current has not been established previously.

has not been established previously.

In order to determine the true peak potential on an oscillogram, the curves for total current and supporting electrolyte current are combined. The curves for the test solution, and for the electrolyte serving as the supporting electrolyte, are photographed by successive exposures on one frame of film. In Fig. 2 are shown the anode wave for Cd in 1 N KCl, the supporting electrolyte current, and the zero line. Such a combined photograph makes it possible to carry out a rapid evaluation of the true values of the current and the potential. In the example given, the apparent shift in peak potential was + 10 millivolts. Subtraction of the supporting electrolyte current from the total current on the oscillogram can be substituted by carrying out the subtraction in the electric circuit of the polarograph itself. Electrical circuits for subtracting currents are well known. It should be pointed out that a bridge setup in its original form is not applicable for subtraction of polarographic currents. In actual fact, let U be the potential applied to the bridge, R_1 and R_2 the load resistances, and C_1 and C_2 the electrolyzers containing test solution and the electrolyte used as supporting electrolyte (Fig. 3). Then the potential drop across the electrolyzers C_1 and C_2 will be, respectively:

$$U_1 = U - i_1R_1; \quad U_2 = U - i_2R_2.$$

But, since for a given bridge, R_2/R_1 = const, while i_1/i_2 for different solutions can change arbitrarily, then

$i_1/i_2 \neq R_2/R_1$ and $U_1 \neq U_2$. Thus, at the very same moment, different potentials will correspond to the minuend and the subtrahend. This destroys the elementary rule for the subtracting of functions, and in this connection will affect the correctness of the result obtained.

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DETERMINATION OF ALUMINUM IN SOLUTIONS CONTAINING FLUORIDE IONS BY MEANS OF 8-HYDROXYQUINOLINE

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Aluminum ions form with fluoride ions complex ions which dissociate only very slightly; of these ions the most stable are AlF^{2+} ($K_{AlF_2+} = 5 \times 10^{-6}$) and AlF_2^+ ($K_{AlF}^{2+} = 8.7 \times 10^{-10}$). Naturally, therefore, ordinary reagents will not react with aluminum ions if fluoride ions are present in solution.

Table 1 contains some results which illustrate the effect of the amount of fluoride ions in solution on the degree of precipitation of aluminum by 8-hydroxyquinoline. In all cases precipitation was carried out under ordinary conditions, in a medium of an acetate buffer solution. The volume was 50 ml in each case. Fluoride ions were introduced as NH_4F.

As is evident from the table, precipitation of aluminum hydroxyquinolate is incomplete at a molar ratio of F:Al as low as 0.25. At a ratio of F:Al = 1, i.e., when all the aluminum in solution is complexed as AlF^{2+}, no precipitate is formed at all. Usually, the test solution is evaporated several times with excess H_2SO_4 or $HClO_4$ until all fluoride ions have been removed; this operation, however, takes up too much time. Attempts have been made to determine aluminum as its 8-hydroxyquinolate in the presence of boric acid which reacts with fluoride ions to form fluoroborates. Unfortunately, the latter are formed in acid solution; under the low acidity conditions which are necessary for precipitation of aluminum hydroxyquinolate, the fluoroborates hydrolyze. Multivalent cations (Fe^{3+}, Ti^{4+}, ZrO^{2+} etc.) are not suitable for complexing the fluoride ions in the case under discussion, since most of these cations are precipitated by the 8-hydroxyquinoline together with the aluminum.

TABLE 1

Effect of Fluoride Ion Concentration on the Degree of Precipitation of Aluminum by 8-Hydroxyquinoline

Molar ratio F:Al	Al	
	taken	found
0.0	0.0286	0.0285
0.25	0.0286	0.0255
0.5	0.0286	0.0191
1.0	0.0286	0.0000

TABLE 2

Determination of Aluminum by Means of 8-Hydroxyquinoline in the Presence of Fluoride and Beryllium Ions (0.0286 g Al taken(F:Al = 1:1)

Be : Al	Al found, g
0.5	0.0281
0.5	0.0282
1.0	0.0286
1.0	0.0286

Beryllium forms very stable complex compounds with fluoride ions ($K_{BeF^+} = 2 \times 10^{-6}$), while at the same time, under the conditions used for precipitating aluminum with 8-hydroxyquinoline (acetate buffer), the beryllium is not precipitated. This led us to the idea of using beryllium ions for complexing the fluoride ions during precipitation of aluminum in the presence of fluoride.

As the result in Table 2 show, beryllium ions enhance the capacity of aluminum to be precipitated with 8-hydroxyquinoline. Even at a molar ratio of Be:Al = 0.5, the effect is very considerable (when lower relative amounts of beryllium are used,the results for aluminum are strongly depressed). However, completely reliable results can be obtained on using a molar ratio of Be:Al = 1. Obviously, the following reaction occurs in solution during the precipitation process:

$$AlF^{2+} + 3Ox + Be^{2+} \rightarrow \downarrow Al|Ox|_3 + BeF^+.$$

Larger amounts of beryllium in solution do not interfere with aluminum determinations.

We suggest that the method recommended by us for the determination of aluminum in solutions containing fluorides can be used in practice under conditions which enable the beryllium to be regenerated from the working solutions; this does not present any great difficulty.

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DETERMINATION OF ALKALI METALS BY A SPECTROGRAPHIC METHOD

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A method was published earlier [1] for spectrographic analysis based on lines located in different parts of the spectrum. As an example, a description was given of the spectrographic determination of the ratio of the concentration of sodium to that of potassium on the basis of the lines Na 3302.3 and K 4044.1. It was assumed that the total sodium and potassium was known and had been determined by a chemical method. By solving the system of equations

$$c_{Na} + c_K = A; \quad c_{Na}/c_K = B,$$

where A is the value found by the chemical method, and B is the value found by the spectrographic method, it is easy to calculate the concentrations of sodium and potassium.

The present work describes a spectrographic method for the determination of the alkali metals in solution, when their sum is not known. The ratio c_{NA}/c_K was determined, as in the previous article, by exciting the spectra in an arc struck between copper electrodes soaked with the test solution, and using the lines Cu 3290.5 and Cu 4022.7.

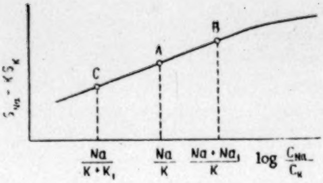
Having constructed a curve within the coordinates $\left(S_{Na} - kS_K; \frac{c_{Na}}{c_K}\right)$ according to a formula obtained previously [1]: $S_{Na} - kS_K = \gamma_{Na} b \log \frac{c_{Na}}{c_K} + \gamma_{Na} \log a$ where the coefficient $k = \frac{\gamma_{Na}\, r}{\gamma_K}$ depends on the contrast factors for the lines Na 3302.3 and K 4044.1, and on the heterogeneity coefficient of the photographic plate r, it is possible to find the ratio of the concentrations c_{Na}/c_K. Let us assume that on the curve for a given solution the coordinates indicated correspond to point A. If a solution of a pure sodium salt or a pure potassium salt is added to the test solution, then obviously the ratio of the concentrations of these metals will change, and points B or C on the curve will correspond to the solution obtained. Knowing the amounts of sodium or potassium salt added, it is easy to calculate their amounts in the test solution. The problem reduces to taking two photographs of the spectra in order to determine the ratio of the concentrations of the alkali elements in the original solution, and in the solution obtained after adding a known weight of one of the metals to the original solution.

Let a known volume of test solution contain (Na) g of sodium and (K) g of potassium. Then the ratio of their concentrations will be

$$\frac{\mathrm{Na}}{\mathrm{K}} = a. \tag{1}$$

If, to this solution is added a standard solution containing a known weight of sodium (Na_1) g, then, obviously, the ratio of the concentrations will change to:

$$\frac{(\mathrm{Na} + \mathrm{Na}_1)}{\mathrm{K}} = b \tag{2}$$



Dividing equation (2) by equation (1), we get $\frac{(Na + Na_1)}{Na} = \frac{b}{a}$, from which

$$Na = \frac{Na_1}{(b/a-1)}. \qquad (3)$$

By substituting the latter in equation (1), we get

$$K = Na_1/(b-a). \qquad (4)$$

If a standard solution of potassium is added to the test solution, then, in a similar way

$$Na/(K+K_1) = d. \qquad (5)$$

Dividing equation (1) by (5), we get $(K + K_1)/K = \frac{a}{d}$, from which

$$K = \frac{K_1}{(a/d-1)}. \qquad (6)$$

By substituting the value of K in equation (1) we get $Na = \frac{aK_1}{(a/d-1)}$.

Having determined the ratio of the concentrations a and b or d, in solution, and knowing the amount of added sodium Na_1 or K_1, it is easy to find the amounts of these elements in the test solution by using either (3) and (4) or (6) and (7) respectively.

Results for the Determination of Alkali Metals in Solution

Actual content, g/ml		Amount found, g/ml		Relative error, %	
Na	K	Na	K	Na	K
0,01045	0,01229	0,01062	0,01252	+1,5	+1,9
0,00925	0,01388	0,00950	0,01372	+2,7	—1,2
0,00833	0,01386	0,00820	0,01408	—1,6	+1,6
0,00635	0,01584	0,00644	0,01563	+1,4	—1,3
0,00565	0,01632	0,00540	0,01654	—2,6	+1,3
0,00333	0,01667	0,00346	0,01637	+3,9	—2,9
0,00278	0,01940	0,00288	0,01931	+3,6	—1,6
0,00247	0,01971	0,00239	0,01995	—3,2	+0,5
0,00222	0,01996	0,00230	0,02027	+3,6	+1,2
0,00182	0,01818	0,00189	0,01849	+3,8	+1,7
0,00159	0,02059	0,00154	0,02043	—3,1	—0,8
0,00148	0,01848	0,00155	0,01858	+4,1	+0,5
0,00131	0,02087	0,00126	0,02071	—3,8	—1,2
Mean arithmetical error				3,0	1,3

In order to check the method we analyzed specially prepared, approximately 5% mixed solutions of sodium and potassium sulfates, and also a 5% solution of potassium sulfate. In order to determine the ratio of concentrations a, 0.5 ml of the standard solution was added to each ml of test solution. The ratios of the concentrations a and d were determined by means of the method described previously [1], after which the content of the alkali metals was calculated by means of (6) and (7).

The accuracy for determination of sodium is about 4%, while for potassium it is about 2% (relative) see Table.

It should be pointed out that the comparatively high accuracy obtained for the spectrographic determination of these elements, despite the large distance separating the analytical lines, is determined in this particular instance by the identity of the analytical lines Na 3302.3 and K 4044.1, and also by the similarity between the physical and physicochemical properties of sodium and potassium salts.

Third components do not affect the experimental results [2].

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A NEW LUMINESCENT METHOD OF MICROCHEMICAL ANALYSIS (CRYSTALLOPHOSPHOR)

COMMUNICATION 2. DETECTION OF TIN

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Most of the qualitative microchemical reactions used for the detection of tin are based on oxidation—reduction reactions. Detection of tin in mixtures containing Fe, Ce, Sb, Bi, As, Hg, etc., is very difficult. At the same time tin can readily be detected by means of potassium iodide on filter paper on the basis of the formation of a crystallophosphor [1].

During a study of qualitative reactions for Tl^+ we noticed that tin ions interfered; the latter, on carrying out the reaction for thallium, produced a bright yellow luminescence [2, 3]. Solutions of sodium and potassium chloride, bromide, and iodide were tested as reagents for tin. Potassium iodide proved to be the best; potassium iodide gives with solutions of tin salts a bright yellow luminescence, the latter develops after drying out the reaction products and illuminating them with an ultraviolet beam. It is of interest to note that the radiation of potassium iodide activated by tin, differs from the radiation of potassium iodide activated by thallium, not only in its color, but also in that the color of the radiation does not change with concentration; only the intensity changes.

In order to establish the sensitivity of the reaction, we used a solution of $SnCl_2$ containing 2.33 mg/ml of Sn^{2+}, and this solution diluted 10, 100, and 1000 times. A bright yellow luminescence was observed with all these solutions, the intensity of the luminescence decreasing with decreasing tin concentration. On diluting further the reaction became indistinct. Thus the limit of identification of tin by this reaction is 0.02 μg of Sn at a limiting dilution of $1 : 5 \times 10^5$. The sensitivity can be increased by using a piece of unglazed porcelain plate instead of paper. When unglazed porcelain is used the limit of identification becomes 0.0002 μg at a limiting dilution of $1: 5 \times 10^6$. The order in which the reaction is carried out has considerable effect on the reaction sensitivity.

Experimental Procedure. A drop of test solution with a volume of 0.001 ml (the diameter of the spot obtained on the filter paper is 3 mm) is placed on a piece of filter paper by touching the paper with a capillary tube containing test solution; some potassium iodide solution is then superimposed on the center of the spot by means of a capillary tube. The potassium iodide solution is allowed to flow out of the capillary so that it covers the whole area of the spot given by the test solution. The drop is dried out and then examined under ultraviolet light. Should a weak luminescence appear the paper is dried further, after which the luminescence should strengthen. The paper should not be overheated; otherwise the potassium iodide will decompose, and the liberated iodine will adsorb the ultraviolet rays and strongly weaken the luminescence, almost to the point of extinguishing it completely. When appreciable amounts of tin are present, an intense yellow luminescence appears at the center of the spot; this is surrounded by a ring of iodine colored red. When the amount of tin is small, the luminescence which is still clearly observed is more diffuse and is redder. When the potassium iodide is placed on the paper before the test solution, a luminescent ring is obtained with a dark center, as a rule.

As indicated previously [1], on carrying out luminescent reactions in which crystallophosphors are formed, interfering elements of two types have been observed. Elements of the first type are those which form similar crystallophosphors (in this instance, these elements are Hg_2^{++}; Tl^+, and, to some extent, Ag^+ and Cu^+). Elements of the second type are those which extinguish the luminescence of the crystallophosphor (in this instance, these elements are Hg^{2+}, Sb^{3+}, As^+, Ag^+, Pb^{2+}, Fe^{3+}. Cu^{2+}). Zinc, cobalt, nickel, germanium, zirconium, gallium, indium, titanium, cadmium, manganese, tungsten, molybdenum, and divalent iron do not interfere with detection of tin.

When Hg_2^{2+} and Hg^{2+} are present the following procedure is adopted: a small drop of potassium iodide solution is placed on the filter paper, this is followed by a drop of the test solution; a further drop of potassium iodide is then added until the mercury iodides have dissolved. When divalent mercury is present, the precipitate dissolves completely and the complex compound formed $K_2[HgI_4]$ does not interfere with detection of tin right up to the point where the solution is saturated with mercury. When univalent mercury is present, on addition of excess potassium iodide metallic mercury is formed, while the precipitate of mercurous iodide is converted into mercuric iodide which is subsequently converted into the complex $[HgI_4]^{2-}$. The metallic mercury formed does not interfere with detection of tin.

It should be pointed out that Hg_2I_2 also exhibits its own characteristic luminescence with a reddish color, but under the conditions used for detecting tin, this reaction is not given so that the mercury does not interfere with detection of tin. Under the conditions used for the reaction for tin, thallium exhibits its own luminescence [2] the color of which depends on concentration; on mixing with the luminescence arising from the presence of tin, the luminescence of thallium acquires almost a pure white color. When the amount of thallium is small, interference on its part can be suppressed by observing the luminescence which arises in ultraviolet with $\lambda = 365$ mμ; at this wavelength the thallium radiation is strongly weakened, while the color of the luminescence arising from the presence of tin changes from a golden-yellow to a greenish-yellow.

When large amounts of thallium are present it is best to remove the tin, even if only half of it, by extraction and then carry out the reaction for tin on the extract.

Sb^{3+}, Bi^{3+}, As^{3+}, Ag^+ and Pb^{2+} ions form strongly absorbing precipitates of iodide. Silver iodide is itself capable of giving a luminescence, but under the conditions used for the reaction for tin, it does not luminesce and does not interfere. Interference from trivalent iron and divalent copper reduces mainly to liberation of elemental iodine. The permissible limiting ratios for the interfering elements during the detection of tin in a drop of 0.001 ml (0.002 μg of Sn^{2+}) are as follows:

$Sn^{2+} : Sb^{3+} = 1 : 100\ 000$
$Sn^{2+} : Bi^{3+} = 1 : 100\ 000$
$Sn^{2+} : As^{3+} = 1 : 10\ 000$
$Sn^{2+} : Ag^{+} = 1 : 30\ 000$
$Sn^{2+} : Pb^{2+} = 1 : 10\ 000$
$Sn^{2+} : Fe^{3+} = 1 : 1\ 000$
$Sn^{2+} : Cu^{2+} = 1 : 1\ 000$

Detection of Tin in Sulfide Rocks. A grain of sulfide rock is placed on a watch glass and treated with concentrated hydrochloric acid, or a mixture of hydrochloric and nitric acids; complete dissolution of the sample is not essential. The solution, which is usually turbid, is transferred onto filter paper by means of a capillary. The procedure given above is then followed; quite satisfactory and distinct results are obtained.

Detection of Tin in Alloys can be carried out in several ways:

a) a grain of alloy is treated on a watch glass with hydrochloric acid and the solution transferred onto filter paper, tin is detected on the latter by the method described above;

b) a very small drop of acid is placed directly on the surface of the alloy and allowed to stand there for some time. So that the drop does not dry out, the spot at which the reaction is carried out is kept moist by breathing on it. The solution is finally transferred onto paper and detection of tin carried out.

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DETERMINATION OF MOLYBDENUM IN ALLOYS BY MEANS OF 8-MERCAPTOQUINOLINE

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8-Mercaptoquinoline (thiooxine) is the sulfur–containing analog of 8-hydroxyquinoline. It has been studied as an analytical reagent by Yu. A. Bankovskii [1, 2].

The selectivity of the reagent in a number of cases makes it possible to determine traces of certain elements in the presence of predominant amounts of other elements, e.g., traces of copper in the presence of large amounts of iron [2].

The problem confronting us was to develop a photometric method for the determination of molybdenum with 8-mercaptoquinoline in multicomponent alloys. 8-Mercaptoquinoline forms a green intercomplex salt with molybdenum which is readily extracted from acid solutions. The composition of the compound has been established by Bankovskii [3] and is expressed by the formula $MoO_2(C_9H_6NS) \cdot H_2O$.

We have checked the method used by Yu. A. Bankovskii [3].

In our experiments the limit of identification proved to be 0.2 γ of Mo at a limiting dilution of 1 : 1,000,000.

The color obtained on extracting 5 γ of Mo from a solution containing 2.5 ml of 2.5 N HCl, 2.5 ml of 10% ascorbic acid, 1 ml of 5% thiooxine hydrochloride (25 ml of concentrated HCl and 75 ml of water), and 1 ml of toluene is identical with the color of 5 γ of Mo (standard solution) extracted under similar conditions, but not containing ascorbic acid; thus, ascorbic acid (in the amount indicated) does not affect the color given by molybdenum with 8-mercaptoquinoline. This means that it is possible to determine molybdenum in the presence of iron.

On extracting 5 γ of Mo in the presence of 2 ml of a saturated solution of oxalic acid* and 2.5 ml of 10% ascorbic acid, there is observed a considerable weakening of the color in comparison with the color obtained when 5 γ of Mo is extracted from a solution not containing oxalic acid and ascorbic acid. During extraction of 5 γ of Mo from 2.5 N HCl in the presence of 2 ml of an 8% solution of thiourea, a pale green color develops, which differs strongly in color from the color of the extract of 5 γ of Mo from a standard solution not containing thiourea. Thus, only ascorbic acid can be used during the extraction of molybdenum in the presence of iron.

In order to determine molybdenum in the presence of tungsten we tested the following: oxalic, succinic, and phosphoric acids. The two latter acids proved to be the most suitable.

Results of the photometric determination of molybdenum with 8-mercaptoquinoline in the presence of other elements are given in Table 1.

The effect of the concentration of HCl and H_2SO_4 on the percentage extraction of 10 γ of Mo with toluene (2 ml) was studied. The amount of reagent in the volume of solution used was not changed during the experiments.

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*Bankovskii recommends using 10 ml of a saturated solution of oxalic acid and 5 ml of 10% ascorbic acid.

TABLE 1

Determination of 1 γ of Mo in the Presence of Other Elements at pH 1

Element present, γ	Ratio Mo:Me, γ	Element present, γ	Ratio Mo:Me, γ
Co^{II}	1 : 3	V^{V}	1 : 100
Cr^{III}	1 : 10	Ni^{II}	1 : 150
W^{VI}*	1 : 10	T^{IV}	1 : 750
Fe^{II}**	1 : 55	Al^{III}	1 : 1800

*In the presence of 0.01 ml of concentrated H_3PO_4.

**In the presence of 2 ml of 10% ascorbic acid.

On extraction of the molybdenum, after shaking the layers up for 3 minutes, the amount of molybdenum remaining in the lower layer of the solution was determined (after destroying the organic reagent).

The experiments (Fig. 1) showed that when the medium has an acidity of 1-10 N HCl, the molybdenum is completely extracted. No experiments were carried out at concentrations in excess of 10 N HCl. Extraction of molybdenum from the sulfuric acid solutions gives satisfactory results starting at an acidity of the solution of 3 N H_2SO_4 (Fig. 1).

TABLE 2

Effect of Time on the Color of the Complex (5 γ Mo, SF-4)

Times, minutes	Optical density, D
–	0.265
15	0.263
30	0.258
45	0.257
60	0.257
75	0.256
90	0.254

The molybdenum was extracted in solution with 2 ml of toluene by shaking for 3 minutes; extraction was carried out in glass cylinders (capacity 30 ml, diameter 14 mm). The green color of the extract containing 5 γ Mo is fairly stable (Table 2).

Solutions containing from 1 to 10 γ of Mo in 1 ml conform to Beer's law.

The method for determining molybdenum with 8-mercaptoquinoline was developed for the purpose of analyzing multicomponent alloys. When the alloys contain tungsten, the latter is kept in solution by adding concentrated phosphoric acid.

An aliquot of chrome-nickel or titanium alloys (0.01 g) is weighed out on a VT-20 torsion balance made by the "Texstil'pribor" factory (scale division 0.02 mg), and provided with two lenses. One of the lenses moves together with the balance needle—the weight indicator. Weighing takes two minutes.

Results of the determination of molybdenum with 8-mercaptoquinoline are given in Tables 3 and 4.

During analysis of alloys containing tungsten it should be borne in mind that the solution obtained can be kept without change for 8 hours, if phosphoric acid is added to keep the tungsten in solution. At the end of this period tungstic acid is precipitated.

Experimental Procedure. 0.01 g of chrome-nickel alloy weighed out on a VT-20 microbalance is dissolved in 5 ml of concentrated HCl contained in a small beaker. If the turning does not dissolved completely, another 2 ml of N HCl is added. When it has dissolved, 5 drops of concentrated HNO_3 is added and the solution heated.

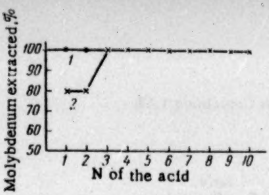

Fig. 1. Relation between extraction of 10 γ Mo and acid concentration: 1) HCl; 2) H_2SO_4.

1.5 ml of concentrated H_2SO_4 is added and the solution evaporated to the appearance of white fumes of sulfuric acid (evaporation is repeated three times until the odor of nitric acid has completely disappeared). On cooling, if any tungsten should be present, 1 ml of concentrated H_3PO_4 is added, followed by 1.5 ml of water and the contents of the beaker heated on an electric hotplate, on a thick sheet of asbestos, until the salts have dissolved completely (overheating should be avoided so as to prevent precipitation of tungstic acid).

The clear solution is transferred to a 100 ml standard flask. 1-3 ml of this solution is pipetted into a graduated colorimeter tube with a capacity of 30 ml and a diameter of 14 mm in order to determine the molybdenum. The reagents are then added in the following order: 2 ml of 2.5 N HCl, 2 ml of water, 1 ml of 10% ascorbic acid* and 1 ml of 5% 8-mercaptoquinoline solution (5 g of reagent is dissolved in 25 ml of concentrated HCl and 75 ml of water). The contents of the tube are then shaken up and 2 ml of toluene added. The molybdenum is extracted by careful shaking for 3 minutes. The phases are allowed to separate. When the method of standard series is used, the colored solution is compared with a series of standard solutions prepared in the same way as the test solution.

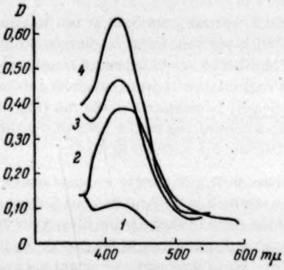

Fig. 2. Light absorption curves for molybdenum with 8-mercaptoquinoline: 1) 5 γ ; 2) 10 γ ; 3) 20 γ ; 4) 30 γ .

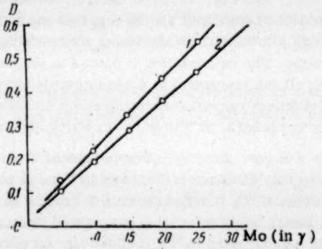

Fig. 3. Calibration curves for the determination of molybdenum in alloys: 1) In chrome-nickel alloys; 2) in titanium alloys.

TABLE 3

Determination of Molybdenum with 8-Mercaptoquinoline in Nickel Based Alloys (aliquot of alloys 0.01 g)

Mo taken,* γ in the aliquot	Mo found, γ	Mo content, %	W content of the alloy, %	Mo found, %	Error, %
12.0	12.20	12,00	—	12.20	1,75
4,90	5,00	4,90	—	5.00	+0,01
3,60	3,60	3,60	—	3,60	—
2,45	2,50	2,45	—	2,50	+0,05
1,20	1,20	1,20	—	1,20	—
0,60	0,60	0,60	—	0,60	—
5.20	5,20	5.20	10.0	5,20	—
3,50	3.30	3.50	10,0	3.30	0,2
2.20	2,20	2,20	12.0	2.20	—
0,90	0,80	0,90	8,0	0,80	0,1

*The molybdenum content of the alloys was established by the thiocyanate method using thiourea.

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*When tungsten is present, 1 ml of concentrated H_3PO_4 is added. In this case ascorbic acid should not be added.

TABLE 4

Determination of Molybdenum in Titanium Alloys Containing 1.5% Chromium (aliquot of alloy 0.01 g)

Mo taken, γ in the aliquot	Mo found, γ	Mo content, %	W added to the alloy, %	Mo found, %	Error, %
8,20	8,40	8,20	—	8,40	+0,2
6,30	6,40	6,30	—	6,40	+0,1
4,20	4,22	4,20	—	4,22	+0,02
2,60	2,60	2,60	—	2,60	—
0,65	0,65	0,65	—	0,65	—
4,50	4,50	4,50	20.0	4,50	—
4,50	4,50	4,50	15.0	4,50	—
4,50	4,50	4,50	10,0	4,50	—
4,50	4,50	4,50	5,0	4,50	—
4,50	4,50	4,50	3,0	4,50	—

For spectrophotometric determination, it is more convenient to extract from 5 ml of test solution, with subsequent addition of all the reagents and 5 ml of toluene. 4.0 ml is pipetted from the extract and filtered through a microfunnel containing a small plug of cotton wool. The filtered liquid is poured into a quartz cuvette (10mm). The null solution is placed in the parallel cuvette; the null solution is prepared under similar conditions, using all the reagents, but excluding molybdenum. The optical density is measured at 420 mμ (Fig. 2). The molybdenum content is determined by means of a calibration curve constructed on the basis of solutions of the chrome-nickel alloy "nimonik" to which known amounts of molybdenum are added (Fig. 3).

For determination of molybdenum in alloys based on titanium, 0.01 g of sample weighed out on a VT-20 torsion microbalance is dissolved in 5 ml of concentrated H_2SO_4 contained in a 50 ml beaker; 7 drops of concentrated HNO_3 is added (when this amount of HNO_3 is used the blue color of the solution disappears completely). The clear, bright solution is evaporated three times to the appearance of sulfuric acid fumes. On cooling, 1.5 ml of concentrated H_3PO_4 is added (for tungsten contents up to 5%). When the tungsten content exceeds 5%, 1.25 ml of a 5% solution of succinic acid is added. The clear solution is transferred to a 100 ml standard flask. The procedure outlined for the analysis of chrome-nickel alloys is then followed. The determination can be carried out visually using the standard series method, or spectrophotometrically (Fig. 2) from a 5 ml aliquot of the solution.

I should like to thank Yu. A. Bankovskii and N. A. Uedinova for donating reagent.

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SPECTROGRAPHIC ANALYSIS BY THE EVAPORATION METHOD

COMMUNICATION 8. ANALYSIS OF ZIRCONIUM*

A. I. Zaidel', L. V. Lipis, and K. I. Petrov**

It is difficult to separate out the weak lines of the spectra of impurities contained in small amounts in zirconium against the background of the multilinear spectrum of zirconium itself. This difficulty can be overcome either by using spectrographs with a high dispersion (this technique has been used by a number of American workers [1, 2]) or by separating the zirconium from the impurities, on the basis of differences in the volatility of the oxides (methods of fractional distillation in a d.c., arc [3]), or on the basis of differences in their chemical properties (spectrochemical methods [4-6]). Of the methods based on fractional distillation the most efficient is the evaporation method [7-10].

Of undoubted promise for the determination of impurities in zirconium dioxide is discharge in a hollow cathode [13]. Its insignificant vapor pressure at comparatively high temperatures [11, 12] has made it possible to have confidence in the successful application of the evaporation method to the determination of impurities in zirconium dioxide. Accordingly, a technique has been developed with precisely this compound in view; other zirconium compounds (nitrate, hydroxychloride, etc.) and also zirconium metal, on calcining in air at 700-800° are readily converted into zirconium dioxide. The conversion of zirconium metal and zirconium compounds into the dioxide leads to an easy solution of the problem of standards, since synthetic standards based on zirconium dioxide are prepared very easily.

The success of the evaporation method depends on the correct choice of the temperatures for heating the samples; the temperature chosen should ensure complete or reproducible separation of the impurities to be determined from the main component of the test sample. The optimum temperature for heating zirconium dioxide at normal pressure in air, and even at reduced pressure is 2000-2100°. At such a temperature the impurities to be determined: B, Bi, Cd, Cr, Fe, K, Na, Li, Ni, Mn, Pb, Sb, Sn, and Si are evaporated off almost completely in 1-1.5 minutes, while Al and Mg are removed to a considerable extent. Evaporation of zirconium dioxide becomes appreciable at temperatures in excess of 2100°. The extent to which some impurities are removed from zirconium dioxide by evaporation was subsequently checked by means of radioactive indicators [9].

The conditions used for spectrographic analysis of the condensate (the parameters of the spark generator, the size of the interelectrode gap, etc.) do not differ from those described in previous communications: $L = 0.15$ μH, $C = 0.01$ μF, $d = 2$ mm. Comparison of the results obtained on evaporating off impurities from ZrO_2 in air and at reduced pressure (about 0.01 mm Hg), showed that with respect to the sensitivity and reproducibility of the determination of all the elements, with the exception of Bi, Cd, Pb, Sb, and Sn, the vacuum variant of the evaporation method is the more advantageous (results for some of the elements are given in Table 1).

During evaporation of the impurities under reduced pressure there are formed even and stable layers of condensate, thanks to which the material passes more efficiently into the discharge zone. A higher condensation coefficient is observed on evaporating the impurities under reduced pressure (the exceptions are Bi, Cd, and Pb for which the condensation coefficient in a vacuum is lowered as a result of a reverse, uncontrolled evaporation of the impurities back from the electrode-receiver) [9].

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*For Communication 7, see J. Anal. Chem. 14, 135 (1959).

**The work described here was carried out in 1952-53.

TABLE 1

Blackening of the Analytical Lines during Evaporation of Impurities at Normal Pressure and at Reduced Pressure

Evaporation conditions	Blackening					
	Al	B	Fe	Mg	Li	Pb
At normal pressure	0.43 ± 0.08	0.89 ± 0.08	0.82 ± 0.07	1.55 ± 0.10	0.91 ± 0.08	0.73 ± 0.07
Under vacuum	0.65 ± 0.07	1.09 ± 0.06	1.02 ± 0.06	1.82 ± 0.10	1.03 ± 0.07	0.29 ± 0.14

Note: 1) The sample of ZrO_2 contained $1 \times 10^{-4}\%$ each of B and Li, $1 \times 10^{-2}\%$ each of Al, Fe, Mg, and Pb. 2) Each blackening value is the mean of 20 measurements. 3) The analytical lines given in Table 2 were used.

TABLE 2

Analytical Pairs of Lines

Analytical line A	Reference line, A	Concentration ranges determined, %
Al I 3082,2	Ga ·I, 2874,2	$1\cdot10^{-3}$—$3\cdot10^{-2}$
Si I 2881,6	2874,2	$1\cdot10^{-4}$—$1\cdot10^{-1}$
Mg I 2852,1	2874,2	$1\cdot10^{-4}$—$3\cdot10^{-2}$
Bi I 3067,7	2874,2	$1\cdot10^{-5}$—$1\cdot10^{-3}$
Sn I 2840,0	2874,2	$1\cdot10^{-4}$—$1\cdot10^{-2}$
Pb I 2833,1	2874,2	$1\cdot10^{-4}$—$1\cdot10^{-2}$
B I 2496,8	Ga I 2500,2	$1\cdot10^{-5}$—$3\cdot10^{-4}$
Cd I 2288,0	2500,2	$1\cdot10^{-5}$—$3\cdot10^{-4}$
Sb I 2598,1	2500,2	$1\cdot10^{-4}$—$3\cdot10^{-3}$
Fe II 2410,5	Co II 2363,3	$1\cdot10^{-3}$—$1\cdot10^{-1}$
Fe II 2382,0	2363,3	$1\cdot10^{-4}$—$1\cdot10^{-2}$
Ni II 2316,0	2363,3	$3\cdot10^{-4}$—$3\cdot10^{-2}$
Mn II 2593,7	Co II 2580,3	$3\cdot10^{-5}$—$3\cdot10^{-3}$
Cr II 2843,2	2580,3	$1\cdot10^{-4}$—$3\cdot10^{-2}$
Li I 6707,8	Analysis was carried out on the basis of the absolute blackening.	$1\cdot10^{-5}$—$3\cdot10^{-4}$
Na I 5889,9		$3\cdot10^{-4}$—$1\cdot10^{-2}$
K I 7664,9		$1\cdot10^{-3}$—$3\cdot10^{-2}$

TABLE 3

Comparison of Results of Determination by Chemical and Spectrographic Methods

Sample No.	Fe, %		Si, %		Ni, %	
	spectrographic	chemical	spectrographic	chemical	spectrographic	chemical
1	$5,3\cdot10^{-2}$	$4,8\cdot10^{-2}$	$3,5\cdot10^{-2}$	$3,3\cdot10^{-2}$	$1,0\cdot10^{-3}$	$1,0\cdot10^{-3}$
2	$1,5\cdot10^{-2}$	$1,4\cdot10^{-2}$	$2,0\cdot10^{-2}$	$2,1\cdot10^{-2}$	$9,0\cdot10^{-4}$	$1,0\cdot10^{-3}$
3	$7,0\cdot10^{-2}$	$6,8\cdot10^{-2}$	$2,2\cdot10^{-2}$	$2,5\cdot10^{-2}$	—	—
4	$3,3\cdot10^{-2}$	$3,0\cdot10^{-2}$	$2,8\cdot10^{-2}$	$2,7\cdot10^{-2}$	$1,1\cdot10^{-3}$	$1,2\cdot10^{-3}$
5	$2,4\cdot10^{-2}$	$2,7\cdot10^{-2}$	$1,2\cdot10^{-2}$	$1,0\cdot10^{-2}$	$6,0\cdot10^{-3}$	$6,8\cdot10^{-3}$
6	$4,5\cdot10^{-2}$	$4,0\cdot10^{-2}$	$3,5\cdot10^{-2}$	$3,5\cdot10^{-2}$	$1,2\cdot10^{-3}$	$1,3\cdot10^{-3}$

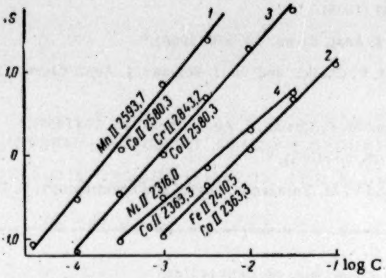

Fig. 1. Calibration curve for the determination of Mn, Cr, Ni, and Fe in Zr.

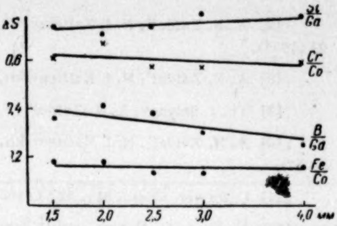

Fig. 2. Effect of interelectrode gap on blackening difference.

In order to eliminate the effect of possible changes in the evaporation conditions, and in excitation of the spectra of the impurities, and also eliminate "third" components, the internal standard method was used. The internal standards used were Co and Ga; these were introduced into both the standards and the test samples in concentrations of 1 × 10^{-2}% which were chosen experimentally. The analytical pairs of lines are given in Table 2, typical calibration curves are shown in Fig. 1.

The homologous character of the analytical pairs of lines was checked experimentally. As examples, on Fig. 2 are shown the curves relating difference in blackening ΔS for certain analytical pairs of lines to the interelectrode gap.

The use of internal standards made it possible to achieve a high degree of reproducibility, this amounted to, for Mn, Cr–8%, B–9%, Fe, Ni, Mg, Si, Bi, Sb, Sn, Pb–10%, Cd–11%, Al, K, Na and Li–20%*. The reliability of the method was confirmed by a comparison of the results of chemical and spectrographic determinations (Table 3).

The sensitivity of the determination of impurities in ZrO_2 is the same as that obtained for the analysis of ThO_2 and BeO [7]. It should be pointed out that this method, as a rule, is 2-3 times, and in some cases, 10 times more sensitive than the method of fractional distillation with a carrier [3], and the method of direct "combustion" of zirconium in various light sources, in which the spectra are recorded by means of spectrographs with high dispersion [1, 2].

SUMMARY

The evaporation method is applicable to the determination of a number of impurities in zirconium dioxide. Reproducible experimental results are obtained by using cobalt and gallium as internal standards.

The vacuum variant of the evaporation method is superior from the point of view of the sensitivity and reproducibility of determination of all the elements tested (with the exception of Bi, Sn, Pb, Cd, and Sb).

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DETERMINATION OF ETHOXY GROUPS IN SOME ORGANO-SILICON AND ALUMINUM COMPOUNDS

E. A. Bondarevskaya, S. V. Syavtsillo, and R. N. Potsepkina

Determination of the ethoxy group content of organosilicon compounds is based on formation of ethyl iodide [1-4]. This method is fairly sensitive and accurate. However, the necessity for a large number of reagents and special apparatus limits its application.

As for organoaluminum compounds no method has been described for determining their ethoxy group content. For this purpose, for certain organosilicon and organoaluminum compounds, we used the properties of these compounds to hydrolyze in the presence of acids or alkalis with the formation of ethanol, which can be quantitatively determined by known methods [5-8], and also by the method of oxidizing it with potassium dichromate [9].

Experimental Procedure. An aliquot of test organosilicon compound (0.12-0.15 g), fused into an ampoule, was placed in a conical flask into which 10 ml of 5% potassium dichromate and 5 ml of sulfuric acid (1 : 1) had been poured beforehand. The ampoule was broken under the level of the solution; the flask was then closed with a stopper fitted with a reflux condenser. The contents of the flask were then heated for 30 minutes on a boiling water bath; the flask was then cooled and 25 ml of 10% iodide solution added; after 5 minutes the liberated iodine was titrated with 0.1 N $Na_2S_2O_3$. A blank was carried out in parallel.

The accuracy and sensitivity of the method were established with various concentrations of ethanol (Table 1).

TABLE 1

OC_2H_5 taken, %	Sample wt., g	OC_2H_5 taken, %	Experimental error, relative %
92,44	0,0510	92,15	0,30
	0,0484	92,23	0,2
47,46	0,1448	47,64	0,4
	0,1084	47,87	0,8
28,61	0,0876	28,59	0,1
	0,0609	28,83	0,7
17,74	0,0938	17,94	1,1
	0,0470	17,96	1,2
10,46	0,2770	10,42	0,4
	0,0909	10,41	0,5
5,01	0,1124	4,99	0,4
	0,1170	5,08	1,4
1,87	0,0929	2,07	10,6
	0,0825	1,91	2,6
0,69	0,1115	0,71	3,0
	0,0992	0,68	1,4
0,10	0,1304	0,11	10,0

TABLE 2

OC_2H_5 taken, %	Sample wt., g	OC_2H_5 taken, %	Experimental error, relative %
11,44	0,1521	11,32	1,0
	0,1806	11,28	2,4
3,51	0,1758	3,44	2,0
	0,2481	3,68	5,0
8,69	0,1910	8,72	0,3
	0,2102	8,58	1,2
1,61	0,1932	1,72	7,0
	0,3532	1,49	7,0
0,53	0,2994	0,50	6,0
0,32	0,3059	0,32	0
	0,3785	0,36	12,0
0,10	0,2710	0,10	0
	0,2452	0,11	10,0

In the course of these experiments we studied whether the oxidation of ethanol obtained by the hydrolysis of diphenyldiethoxysilone, and subsequently diluted with polymer free from ethoxy groups, is quantitative (Table 2).

TABLE 3

Test material	Sample, wt.	OC_2H_5 found, %	Experimental error, relative %
Triethoxysilane	0,0721	82,66	0,4
82,31% OC_2H_5	0,0701	82,43	0,1
Tetraethoxysilane	0,1589	85,70	0,9
86,53% OC_2H_5	0,1148	85,76	0,8
Methylfluorobenzene	0,1489	39,18	0
diethoxysilane	0,1384	39,89	0,9
39.2% OC_2H_5			
Diphenyldiethoxysilane	0,1196	33,29	0,6
33,08% OC_2H_5	0,1478	33,19	0,2
Phenyltriethoxysilane	0,1384	55,84	0,8
56,25% OC_2H_5	0,1391	55,94	0,5

TABLE 4

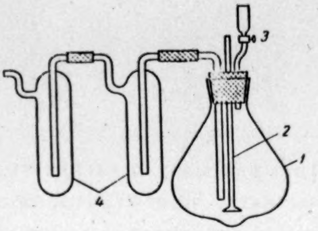
Test material	Sample wt., g	OC_2H_5, %	Experimental error, relative %
Triethoxyaluminum,	0.0731	78.98	2.0
calculated	0.1108	78.45	2.8
80.63% OC_2H_5	0.1142	79.92	0.9
	0.0996	79.50	1.0

TABLE 5

Wt. of triethylaluminum, g	OC_2H_5 obtained by	
	$K_2Cr_2O_7$, %	HI, %
0.1135	2.24	–
0.1115	2.18	–
0.0811	2.72	–
0.0395	–	2.29
0.0468	–	2.59
0.0244	–	2.76

From the results given in Tables 1 and 2 it is evident that the sensitivity of the method amounts to 0.1-0.3%; while the accuracy is up to about 12% relative. The method indicated was used for the analysis of organosilicon compounds with differing contents of ethoxy groups (Table 3).

The principle of the method described was extended to the determination of diethylethoxyaluminum as an impurity in triethylaluminum. Since triethylaluminum is oxidized violently in air, the method was modified, mainly with the aim of choosing conditions for preventing the triethylaluminum from coming into contact with air during sampling and during hydrolysis. The samples of triethylaluminum were taken in thin-walled ampoules which had been placed beforehand in a vacuum desiccator to remove the air inside them and fill them



with nitrogen free from oxygen. The bulb of an ampoule was then heated slightly and its tip rapidly immersed through an opening in the stopper of the tube containing test material. During this process nitrogen free from oxygen was bubbled vigorously through the sample. The filled ampoule was sealed off and transferred to the flask of the apparatus. Nitrogen was passed through the flask 1 (diagram) containing the sample for 12-20 minutes in order to expel the air; the ampoule was broken with the rod 2, and water added dropwise from the dropping funnel 3 until the material had decomposed completely. After this, the contents of flask 4, into which water had been poured before commencing the experiment, was quantitatively transferred into the flask; to the same flask was then added 5 ml of 5% $K_2Cr_2O_7$ and 3 ml of H_2SO_4 (1 : 1); the flask was closed with a stopper fitted with a reflux condenser, and heated on a water bath for 30 minutes; the procedure followed subsequently was the same as that indicated above. This method was used for determining the ethoxy groups in triethoxyaluminum (Table 4), and also for determining diethylethoxyaluminum as an impurity in triethylaluminum. During these determinations a comparison was made of the method described, with the method of determining ethoxy groups by means of hydrogen iodide [3] (Table 5).

From the results given in Table 5 it is clear that both methods give reproducible values.

SUMMARY

A method has been developed for determining ethoxy groups in certain organosilicon and organoaluminum compounds; it is based on the hydrolysis of the compounds examined and subsequent quantitative determination of the alcohol formed.

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QUANTITATIVE DETERMINATION OF THE COMPOSITION OF THE COPOLYMER OF TETRAFLUOROETHYLENE WITH TRIFLUOROETHYLENE BY INFRARED SPECTROSCOPY

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The method of determining the composition of the copolymer of tetrafluoroethylene ($CF_2 = CF_2$) with trifluoroethylene ($CF_2 = CFH$) is based on differences in the absorption spectra of the polymers of tetrafluoroethylene and trifluoroethylene in the region of the absorption of C-H bonds. Measurements were carried out on an IKS-11 apparatus with a LiF prism (for the region 2900-3100 cm^{-1}) and a NaCl prism (for the region 750 cm^{-1}). The absorption band of the C-H bonds in the sectors of polytrifluoroethylene and the copolymer is observed at 2987 cm^{-1}. The band at 2987 cm^{-1} and also the spectrum for polytetrafluoroethylene in this region are shown in Fig. 1. Since polytetrafluoroethylene is transparent in this region, all the absorption of the copolymer is caused by one of its components—trifluoroethylene.

The experimental procedure consists of the following. From the spectra of films of polytrifluoroethylene a curve is constructed relating the optical density at the maximum of the band at 2987 cm^{-1}(D_0) and the thickness of the films in d_1 microns (Fig. 2). The value of the optical density for 1 μ thickness of film is given by $D = 0.170$. The optical density of the copolymer at the maximum of the band 2987 cm^{-1} is then determined; from the curve (Fig. 2) the effective thickness d_1 of trifluoroethylene in the film of copolymer is determined.

The value $d_1/(d-d_1)$ (where d is the thickness of the copolymer film) gives the ratio of the effective thicknesses of trifluoroethylene and tetrafluoroethylene in the given sample of copolymer.

In order to find the ratio of the number of molecules of one component to the number of molecules of the other component (i.e., the ratio of the volume of the monomers composing the copolymer), it is necessary to multiply $d_1/(d-d_1)$ by K which is equal to $\rho_1/\rho_2 \cdot M_2/M_1$, where ρ_1, ρ_2, M_1, and M_2 are the density and molecular weight of trifluoroethylene and tetrafluoroethylene respectively. In our case K approximates to 1; accordingly, the ratio of the effective thicknesses gives the ratio of the number of molecules of the monomers which have been copolymerized, while the content of one of the components of the copolymer, e.g., trifluoroethylene (c_1) is given as a percentage by: $c_1 = d_1/d \cdot 100\%$.

The use of this technique is based on two assumptions: first, it is assumed that the volume of the copolymer is made up additively from the volumes of the polytetrafluoroethylene and polytrifluoroethylene; second, it is assumed that the absorption for one C-H group in the spectra of polytrifluoroethylene and copolymer is the same. The correctness of these assumptions is confirmed by the good results obtained during the analysis of standard samples of the copolymer by the suggested method.

The standards used for checking the method suggested were samples of copolymer whose composition had been determined by analysis of the gaseous mixture of monomers (i.e., mixtures of tetrafluoroethylene and trifluoroethylene).

The spectra of the monomers (shown in Fig. 3 [1]) were used for analyzing the gaseous mixtures. Trifluoroethylene has an absorption band at 750 cm^{-1}. Since tetrafluoroethylene does not absorb at this wave length, this band was chosen for constructing calibration curves relating optical density of the mixtures at the absorption

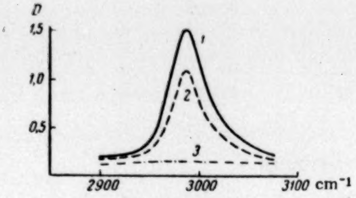

Fig. 1. 1) Polytrifluoroethylene; 2) copolymer of tetrafluoroethylene and trifluoroethylene; 3) polytrifluoroethylene.

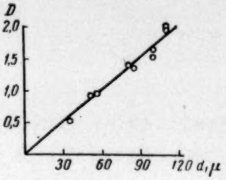

Fig. 2.

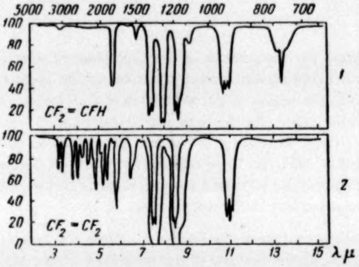

Fig. 3. 1) Trifluoroethylene; 2) tetrafluoroethylene.

Trifluoroethylene Content of Standard Samples of Copolymer, %

On the basis of the band intensity at the maximum	On the basis of analysis of gaseous mixtures of the monomers	On the basis of integral absorption
44.5	43.0	43.5
44.2	39.0	38.5
57.2	59.4	52.5
73.7	74.1	69.5
26.3	23.2	24.0

maximum to the trifluoroethylene concentration of the mixtures. The calibration curve (Fig. 4) has two linear sections with a break in the concentration range 20 to 40%. The concentration of trifluoroethylene is plotted along the abscissa while the values of the optical density of the band at 750 cm^{-1} are plotted along the ordinate. It should be pointed out that a curve with this shape is characteristic for cases where one of the components of a mixture has a C-H bond. Probably the non-linearity can be explained by the formation of association between the molecules of the gas. The spectra of the gaseous mixtures of the monomers were obtained under atmospheric pressure; the mixtures were placed in a cuvette with a layer thickness of 1 cm and with windows made of NaCl.

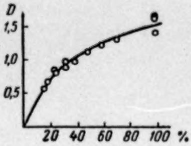

Fig. 4.

Results obtained during a comparison of the given method with the values of the standards are given in the Table. The first column of the Table contains the values of the trifluoroethylene concentrations, in percentages, for the standard samples, as determined by the method suggested. The second column contains the values of the trifluoroethylene concentrations for the same samples, but determined by analysis of the gaseous mixtures. The agreement between the two sets of results can be regarded as satisfactory. This indicates that the intensity of the absorption band for the one C-H group of trifluoroethylene is maintained in the copolymer.

A check on the determination of the composition of the copolymer on the basis of the integral intensity of the absorption band instead of on the basis of the absorption at the maximum, showed that the same direct proportionality exists between the integral intensity of the band at 2987 cm^{-1} and the film thickness. Results of this check are given in the third column of the Table.

Films of varying thicknesses were used for determining the composition of each of the copolymers tested. The scatter of results obtained during this work did not exceed 10%.

I should like to thank V. M. Chulanovskii for his interest in the work, G. I. Lapotinikova for help with the measurements, and S. G. Malkevich for samples of copolymers and mixtures of gases.

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A METHOD FOR THE QUANTITATIVE DETERMINATION OF ACRYLONITRILE BY MEANS OF PIPERIDINE

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The M. V. Lomonosov Moscow State University

For the quantitative determination of acrylonitrile we have used its reaction with piperidine $CH_2(CH_2-CH_2)_2NH + CH_2=CH-CN \rightarrow CH_2(CH_2-CH_2)N-CH_2CH_2CN$, which proceeds quantitatively in the presence of catalytic amounts of acetic acid. The β-(N-piperidyl)-propionitrile which is formed possesses basic properties and can be titrated with acid. An aliquot of acrylonitrile is treated with excess piperidine for 30 minutes at room temperature. Excess piperidine is bound by means of acetic anhydride, while the β-(N-piperidyl)-propionitrile is titrated with a solution of hydrochloric acid in methanol using a mixed indicator of methyl red and methylene blue. The amide and acetic acid which are formed by the interaction of piperidine and acetic anhydride do not interfere with the titration. Prior to analysis, the acrylonitrile is dried with calcium chloride and distilled. Purified dioxane is used as solvent.

Since piperidine, despite careful purification, may still contain impurities which can react with acid, and which cannot be bound with acetic anhydride, a blank is carried out. Acrylonitrile is also determined by the sulfite method for comparison [2]. Acrylic acid and its esters interfere with acrylonitrile determination. Ethylenecyanhydrin does not appear to interfere.

Sample wt., mg	Acid used for titration, ml	Acrylonitrile found, %	
		by the piperidine method	by the sulfite method
43.12	16.23	99.84	99.88
50.68	19.10	99.90	–
50.68	19.08	99.89	–
42.00	15.84	100.00	–
51.10	19.20	99.64	–
31.90	12.00	99.81	–

0.05 N hydrochloric acid in anhydrous methanol is prepared by dissolving concentrated hydrochloric acid in anhydrous methanol. The indicator used is methyl red–methylene blue (0.2 g methyl red and 0.04 g methylene blue, 60 ml methanol and 40 ml distilled water).

The determination is carried out by introducing 5 g of piperidine into a 50 ml standard flask and diluting to the mark with dioxane; the solution is then thoroughly mixed. 5 ml of this solution is pipetted into a 100 ml flask fitted with a ground glass stopper, and 30-50 mg of acrylonitrile in a sealed ampoule introduced; the ampoule is broken with a glass rod; the rod is rinsed with dioxane and 0.2 ml of 50% acetic acid added to the mixture. The solution is shaken up and then allowed to stand for 30 minutes; 5 ml of acetic anhydride is added dropwise from a buret, followed by 3 drops of indicator solution, and the solution finally titrated with 0.05 N hydrochloric acid in methanol to the appearance of an intense raspberry color. A blank is carried out at the same time. Results for the determination of acrylonitrile are given in the Table.

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DETERMINATION OF DIBUTYLPHOSPHORIC, MONOBUTYLPHOSPHORIC, AND PHOSPHORIC ACIDS BY MEANS OF PAPER CHROMATOGRAPHY

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During a study of the radiolysis of tributylphosphate, of considerable interest was the quantitative determination of dibutylphosphoric (DBP) and monobutylphosphoric (MBP) acids; the latter are formed under the action of radiation, and show an essential effect on the processes of extraction separation of thorium, uranium, and fission products [1].

Partition chromatography on paper can be used for determining the yields of DBP and MBP. In many cases, this technique permits analysis of very small amounts of material [2-4].

Separation of mixtures on paper depends on a number of factors: adsorption on the surface, ion exchange, and partitioning between solvents. Of these, the most important factor is the latter; accordingly, the correct choice of solvent determines the success of the chromatographic separation.

Separation of DBP and MBP is most complete on using chloroform and alcohols.

In order to ensure constant values of the partition coefficients, it is usual to carry out chromatographic separation of acids in a medium containing an acid or a base [5]. We used mixtures of a base with alcohols, since DBP and MBP hydrolyze to a lesser extent in alkaline solutions [6]. In order to cut down the time of chromatographic separation, the solvent was raised to a height of 15-20 cm. For values of the height less than 15 cm, the R_f value was found to depend on the path through which the solvent passed; this is explained by the existence of a gap between the solvent front and the point on which the acid is applied.

The setup used for chromatographic separation was a glass cylinder 30 cm tall, with an internal diameter of 13 cm; it was fitted with a ground glass lid and a holder for six paper strips. A cell (Petri dish) containing the organic solvent was placed on the bottom of the cylinder. Paper made by the Volodarskii factory (GOST 5621) was used for chromatographic separation; the paper was washed with 0.1 N oxalic acid, and then with water, and, finally with alcohol.

0.02 ml of the solution of acids was placed by means of a capillary on strips of paper 2.5 cm wide, at a distance of 2 cm from the edge of the paper.

After the spots had dried out, the strip was fastened in the cylinder and the chromatograms allowed to run for 3-4 hours.

The following solvent mixtures were used for the separation:

1. Butanol–methanol–water (4 : 1 : 2).
2. Isoamyl alcohol– pyridine–25% ammonia solution (6 : 14 :20).
3. Chloroform–methanol–H_2O (4 : 5 : 1).
4. Propanol– 25% ammonia solution–water (6 : 1 : 3).
5. Methanol–25% ammonia solution–water (6 : 1 : 3).

TABLE 1

Solvent	R_f value		
	dibutylphosphoric acid	monobutylphosphoric acid	H_3PO_4
4	0.81–0.88	0.52–0.55	0.35–0.26
3	0.93–0.96	0.73–0.75	0.21–0.24
2	0.86–0.89	0.53–0.57	0.24–0.18
1	0.72–0.77	0.47–0.53	0.22–0.27
5	0.93–0.88	0.68–0.74	0.47–0.53

A mixture of 5 ml of 60% perchloric acid, 10 ml of 1 N hydrochloric acid, and 25 ml of 4% ammonium molybdate, diluted to 100 ml with water was used for establishing the position of the acid spots on the paper [4]. The chromatograms were sprayed with the mixture, dried in warm air, and heated for 7 minutes at 85°; they were then left in air in order to get saturated with moisture, and finally suspended for 5-10 minutes in a vessel containing H_2S. The developed spots were cut out, wet oxidized with a mixture of concentrated H_2SO_4 and HNO_3 (1 : 1) and the orthophosphate determined [6, 7].

Solutions of the independent components, as well as a solution of a mixture of dibutylphosphoric, monobutylphosphoric, and phosphoric acids were used for the experiments. The R_f values were calculated as the ratio of the distance through which the components had passed through to the distance through which the solvent had passed.

TABLE 2

Solvent	Dibutylphosphoric acid, γ			Monobutylphosphoric acid, γ			H_3PO_4			Total P, γ		
	taken	found	difference	taken	found	difference	taken	found	difference	taken	found	difference
1	31	33	+ 2	19	16	- 3	14	16	+ 2	64	65	+ 1
4	31	30	- 1	19	18	- 1	14	16	+ 2	64	64	0

Identification of the components on a chromatogram was carried out by comparison with the rate at which a "marker" moved. The values of the coefficients for the rate of movement of various solvents are given in Table 1.

Variations in the R_f values depend, presumably, on differences in the density of the filter papers and on temperature variations.

It should be pointed out that in the process of deciding on the ratios of the components in the system chloroform–methanol–water, under the conditions we used, we established that on using chloroform saturated with water, dibutylphosphoric acid (concentration 10^{-2}N) remains on the paper at the point where it was placed, probably as the result of its adsorption by the filter paper.

The fact that dibutylphosphoric acid is held by the paper can presumably be used for separating dibutylphosphoric acid from tributylphosphate.

Results of experiments on the quantitative determination of the components of the mixtures are given in Table 2.

The results which we obtained lead one to conclude that dibutylphosphoric, monobutylphosphoric, and phosphoric acids can be separated by partition chromatography on paper.

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V. I. KUZNETSOV

(On his fiftieth birthday)

Doctor of Chemical Sciences Vitali Ivanovich Kuznetsov, one of the leading Soviet analytical chemists, an outstanding specialist in the application of organic reagents, the author of more than 200 scientific papers, and a professor, recently celebrated his fiftieth birthday.

V. I. Kuznetsov was born on the 21st of April,1909 in the village of Uyar in Krasnoyarsk province. In 1930 he finished at Tomsk State University. He then worked in the All Union Institute of Mineral Raw Material and in other scientific institutions. At present V. I. Kuznetsov heads the laboratory of organic reagents of the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR.

The main and constant theme of his research is the development and study of organic reagents for different analytical purposes: for color reactions, extraction, coprecipitation. On the basis of his work dozens of methods which have found wide practical applications have been developed in the USSR and abroad. Mention may be made of thoron, arsenazo (uranon) and their analogs anthrazo, phenazo, phenysulfazo, anthraxas, stilbazo, etc., among those reagents which he has developed.

V. I. Kuznetsov has done a great service in developing the theoretical bases of extraction separation of the elements. He was one of the first to introduce ideas regarding the various mechanisms of extraction, and to suggest a classification for the numerous extraction processes. His review article on extraction enjoys popularity among chemical specialists. V. I. Kuznetsov has also done a considerable amount of work in developing new practical techniques for the extraction separation of the elements. He has suggested a collection of low melting extractants which can be used for extracting elements over a wide acidity range.

V. I. Kuznetsov has developed a new, efficient method for coprecipitating ultra-small amounts of more than 30 elements by means of organic coprecipitants.

Under his guidance a new spectrophotometric method has been developed—thermospectrophotometry; the latter technique is of considerable importance for continuous automatic control of production.

V. I. Kuznetsov has carried out some original work in the field of organic synthesis, using complex chelate compounds. The methods he developed have made it possible to increase the reactivity of materials, and to carry out syntheses which were hitherto impossible or presented considerable experimental difficulties.

In the theory of action of organic reagents, mention should be made of the theory of the similarity between the action of organic and inorganic reagents, which has made it possible to forecast the properties of new reagents; the theory of the colors of reagents and their complexes; and also research on the properties of characteristic atomic groups and the influence of the structure of organic reagents on the stability of the complex compounds they form. V. I. Kuznetsov has suggested a new, objective method for evaluating the relative stability of complexes.

Kuznetsov has carried out a lot of work on popularizing new scientific ideas and methods in analytical chemistry so that they are adopted as rapidly as possible in industry.

The Commission on Analytical Chemistry and the Editorial Board of the Journal of Analytical Chemistry, Acad. Sci. USSR, wish V. I. Kuznetsov many years of fruitful work for the benefit of our country.

THE ANALYTICAL CHEMISTRY SECTION AT THE AT THE VIII MENDELEEV MEETING ON GENERAL AND APPLIED CHEMISTRY

(March 16-23,1959)

About 300 people from various scientific research institutes, colleges, and industrial enterprises, and also scientists from China, Bulgaria, Czechoslovakia, Poland, Hungary, and Italy took part in the work of the analytical chemistry section. About 70 reports were heard at the meetings.

In his introductory address I. P. Alimarin pointed out the successes achieved, and the modern problems of analytical chemistry.

Reports on the basic fields of analytical chemistry were widely presented: physical and physicochemical methods of analysis, the use of new organic reagents, elemental organic microanalysis, chromatographic analysis and the use of labeled atoms in analytical chemistry.

I. V. Tananaev reported on the use of the techniques of physicochemical analysis in heterogeneous systems for solving a number of the problems of analytical chemistry.

In his report on modern tendencies in the use of organic reagents, V. I. Kuznetsov, in addition to noting the successes achieved, pointed out a number of the drawbacks in the search for, and during the synthesis of, the necessary reagents. A. K. Babko, taking as examples the halogen and thiocyanate complexes, showed the connection between the stability of complexes and the position of the corresponding central atoms in D. I. Mendeleev's periodic system.

V. M. Peshkova and V. M. Bochkova reported on the stability of the oximates of Cu, Co, and Ni as a function of the structure of the oxime molecule. V. F. Toropova reported on the twofold character of the reaction of certain compounds during complex formation. The address given by Z. F. Shakhova and his coworkers A. I. Kokorina and N. A. Polotebnova touched on questions of using heteropolyacids in analytical chemistry.

A large number of reports was devoted to the application of new organic reagents in analysis. Thus, dialkyl- and diaryldithiophosphoric acids (A. I. Busev and M. I. Ivanyutin) have been used for separating a number of elements, while arylarsonic and arylphosphinic acids have been used for the same purpose (A. I. Portnov). R. P. Lastovskii and coworkers reported on some properties of new complexons. The attention of the audience was drawn by the reports of V. A. Nazarenko, G. G. Shitateva, and A. I. Kononenko on the photometric determination of a number of elements using fluorone derivatives. A. I. Cherkesov reported on the use of the "halochrome" phenomenon in analytical chemistry.

Of undoubted interest was the report of B. M. Dobkina and T. M. Malyutina on the determination of tantalum by the method of differential spectrophotometry. Deserving of attention was the communication by Yu. V. Morachevskii and I. A. Stolyarova on new, highly sensitive methods of analysis using an ultraviolet microscope.

Several reports were devoted to methodological and theoretical questions in spectrographic analysis (N. F. Zakharii and G. A. Sheinin,, É. E. Vainshtein and coworkers).

Significant successes have been achieved in improving flame photometry. (N.S.Poluéktov and M.N. Nikonov).

Several reports were devoted to the polarographic determination of the elements. (S. I. Sinyakova, Z. B. Rozhdestvenskaya and I. A. Yarova, and Ya. P. Gokhshtein). I. D. Panchenko and Yu. S. Lylikov and coworkers gave some new results on the application of solid electrodes. Kemulya (Poland) gave a very interesting report on a polarographic method for the determination of traces of metals using a suspended drop. J. Semerano (Italy) reported on the use of polarography and spectrophotometry for establishing the nature of the Me-C bond in organometallic compounds.

E. Minchevskii (Poland) discussed titration in non-aqueous media.

The communication by N. I. Udal'tsova and P. N. Palei was devoted to the use of amperometric titration with two electrodes in uranium and thorium chemistry.

Considerable attention was devoted to chromatographic research.

M. M. Senyavin demonstrated the possibility of forecasting the conditions for chromatographic separation of elements on the basis of the position of the elements in the Mendeleev periodic system. T. A. Belyavskaya reported on the use of ion exchange for studying the state of materials in solution.

Interesting reports were heard on the chromatographic separation of a number of elements (A. S. Vernidub and V. I. Petrashen'), on the problem of regulating the properties of ion exchange resins (N.G. Polyanskii), on the chromatographic detection of sulfanilamide preparations in the liquids of organisms (F. M. Shemyakin and coworkers), and also on the use of high polymers in chromatographic analysis (G. L. Starobinets and coworkers). Two reports were devoted to gas chromatography (A. A. Zhukhovitskii and N. M. Turkel'taub, and G. Shai-Hungary).

Several reports were devoted to the use of radioactive isotopes for studying the processes of complex formation by a chromatographic method (D. I. Ryabchikov and coworkers). for studying the mechanism of the coprecipitation of the ions of rare metals with sulfides (N. A. Rudnev), and for the determination of rare elements by the method of isotopic dilution (I. P. Alimarin and G. N. Bilimovich).

Of the communications on elemental organic microanalysis, one should point out the reports of M. O. Korshun, N. E. Gel'man, and V. A. Klimova and coworkers on the development of rapid micromethods with simultaneous determination of several elements on one aliquot of boron-, fluoro- and silico-organic compounds.

Of the reports of foreign scientists, of particular interest was the communication by Professor Liu Ta-kang (China) on the present state of research on rare elements in China. The professor brought a gift of a collection of rare earths for the Soviet Union.

The proceedings at the various sessions were lively; valuable suggestions and recommendations were put forward.

G. N. Bilimovich

THE PRECISION OF SPECTROPHOTOMETRY

COMMUNICATION 2. THE DIFFERENTIAL METHOD AND THE OPTIMUM CONDITIONS FOR SPECTROPHOTOMETRY*

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Many papers have been devoted to the question of the precision of spectrophotometry. These papers have dealt with the sources of error, have established the optimum experimental conditions, and established the maximum accuracy which is possible on a given spectrophotometer. The present article only deals with the photoelectric method of spectrophotometry. The equations which have been taken from cited papers have been simplified and given in unit terms and designations, optical density being used mainly.

A Brief Review of the Equations for Precision in Spectrophotometry

Absolute method. Twyman and Lothian [1] in 1933 were the first to establish the optimum optical density which will ensure maximum experimental accuracy. From the expression for the optical density they obtained a relation between errors in measuring the optical density ΔD and the transmission ΔT:

$$\Delta D = \frac{0,43\,\Delta T}{T} \tag{1}$$

(T is the transmission).

Using Beer's law

$$D = uc, \tag{2}$$

where D is the optical density, c is the concentration of the absorbing component, and u is the slope of the concentration straight line, the error in determining the concentration was determined. The relative error of spectrophotometric analysis is determined by the following equation:

$$\frac{\Delta c}{c} = \frac{\Delta D}{D} = \frac{0,43\,\Delta T}{T}. \tag{3}$$

Twyman and Lothian regarded ΔT as the smallest change in transmission which can be measured. Accordingly, Δc/C is the minimum possible error. The authors only took into account the errors of the electrical setup, and were of the opinion that ΔT does not depend on the transmission itself, T. Under these conditions the experimental error has a minimum value at $D_{\text{expt.}} = 0.43$.

The differential method. In 1937 Kortum [2] first described a new precision method of spectrophotometry which later was named the "differential" method.

The method consists of measuring the optical density of a solution of the sample, not relative to the pure solvent (or solution of reagents) with a zero or near zero absorption, but relative to a standard solution, containing a known amount of the test component complexed as a colored compound with the same reagents as those used for the test solution, the optical density of the standard solution used being high (about 2.0).

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*Communication 1, see J. Anal. Chem. 14, 388 (1959).

The method of measurement on the spectrophotometer remains the same as in the absolute method, but the zero standard which is placed in the light beam on setting up the optical density scale at zero is not a solvent plus reagents as in the absolute method, but a standard solution of the test component in the form of a colored compound. Under such conditions the slit width is considerably increased so that the light beam falling on the photoelement does not change as the result of its absorption by the solution.

Of articles devoted to developing the differential method, mention should be made of the work of Bastian [3-6], and, particularly, Hiskey [7-11]. Russian literature contains only individual brief mention of the differential method in a number of articles of a review nature [12-14]. This method has hardly entered into laboratory practice at all in Russia.

For the rest of this section D and T will designate the readings of the spectrophotometer, and not the absolute values of the optical density and transmission (except in special, specified instances).

The optical density, i.e., the reading of the spectrophotometer D, measured in the differential method, is the difference between the absolute optical densities of the sample D_{sample} and the zero standard D_0. Using Beer's law, we get

$$D = D_{\text{samps}} - D_0 = uc - uc_0, \tag{4}$$

where c_0 is the concentration of the absorbing component in the zero standard, and $\underline{c}$ is the concentration of this component in the solution being measured photometrically.

From equation (4), and using equation (1), we get the relative experimental error in determining the concentration:

$$\frac{\Delta c}{c} = \frac{\Delta D}{D_{\text{samps}}} = \frac{0{,}43\,\Delta T}{T\,(D_0 + D)}\,. \tag{5}$$

Hiskey considered that the error in the transmission scale ΔT (which he regarded as a double mean deviation) is a constant, and is independent of the reading itself. On this basis, Hiskey showed that the experimental error is smaller, the higher the optical density of the zero standard, and that the optimum reading of the optical density scale, for which the accuracy of the analysis is a maximum, is expressed by the equation

$$D_{\text{expt.}} = 0.43 - D_0. \tag{6}$$

For optical densities of the zero standard greater than 0.43, Hiskey considered a reading of $D = 0$ as the optimum (since the spectrophotometer scale does not have negative values of optical density).

It should be observed that all the equations for the differential method, for zero values of D_0 and c_0, hold true for the absolute method. Accordingly, henceforth, we shall regard the differential method as the most general method.

The Optimum Conditions for Spectrophotometric Analysis

We have shown earlier [15] that the error in measuring the reading of the transmission scale depends on the reading T itself. During measurements on a spectrophotometer with electrical compensation, only the instrumental error $\sigma_{T_{\text{inst.}}}$ is a constant, this error being the result of the insufficient sensitivity of the spectrophotometer, and the visual errors of measurement. The cuvette error which is determined by the non-reproducibility of the state of the cuvette is strongly dependent on T. It is necessary to establish the optimum conditions, taking the latter error into account.

In order to obtain a correct solution of the problem confronting us, it is necessary to analyze the relative mean square error of an analysis:

$$\frac{\sigma_c}{c} = \frac{\sigma_D}{D_0 + D} = \frac{0{,}43\,\sigma_T}{T\,(D_0 + D)}. \tag{7}$$

In the case where the instrumental error $\sigma_{T_{\text{inst.}}}$ is independent of T (e.g., when working with a spectrophotometer with electrical compensation), the error in measuring the readings of the transmission scale is expressed by the following equation [15]:

$$\sigma_T = \sigma_{T_{\text{in.}}}\sqrt{1+\left(\frac{T}{T_{\text{lim}}}\right)^2}, \qquad (8)$$

where

$$T_{\text{lim}} = \frac{\sigma_{T_{\text{in.}}}}{\sigma_{T_{\text{K}}}} \qquad (9)$$

is the limiting reading of the transmission scale, for which the error in the reading of the transmission scale caused by the non-reproducibility of the state of the cuvette is equal to the instrumental error.

$\sigma_{T_{\text{cuvette}}}$ is the mean square deviation of the transmissions of the cuvette relative to one another when the cuvette is filled up repeatedly with the same solution.

For a given determination (constant sensitivity of the spectrophotometer, and the same number of individual readings, and the same method of preparing the cuvette) the limiting reading of the scale is a constant.

Substituting equation (8) in equation (7) we get:

$$\frac{\sigma_c}{c} = z = \frac{0{,}43\,\sigma_{T_{\text{in.}}}\sqrt{1+\left(\frac{T}{T_{\text{lim}}}\right)^2}}{T\,(D_0+D)}. \qquad (10)$$

It follows from this equation that in order to increase the precision of an analysis it is necessary to work at a fairly high spectrophotometer sensitivity (in order to lower $\sigma_{T_{\text{inst.}}}$), to maintain the absorption of the cuvette a constant (in order to increase T_{limit}), and to use a zero standard with maximum optical density D_0.

These conditions for increasing the experimental accuracy have been noted earlier.

In Fig. 1 is shown the theoretical relationship between the function z and the readings of the optical density scale; $T_{\text{limit}} = 10$ (dotted lines) means that $\sigma_{T_{\text{cuvette}}}$ is negligibly small, i.e., this curve for $\sigma_T = \sigma_{T_{\text{inst.}}} = \text{const}$. In general, for high values of T_{limit}, equation (10) transforms into Hiskey's equation. But usually, T_{limit} is considerably smaller ($T_{\text{limit}} < 10$). It is precisely for this case that the curves with complete lines have been drawn ($T_{\text{limit}} = 1/4$). These curves, as is evident from the diagram, differ considerably from Hiskey's curve both with respect to the magnitude of the function and with respect to the position of its minimum. At higher values of D the curves merge into each other, since the instrumental error becomes the dominating factor [15].

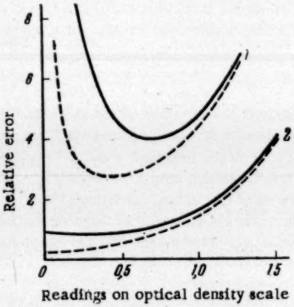

Fig. 1. Precision curves. $\sigma_{T_{\text{inst.}}} = 1$ (arbitrarily). Full lines – $T_{\text{limit}} = 1/4$ dotted lines – $T_{\text{limit}} = 10$. 1) Absolute method; 2) differential method ($D_0 = 2$).

Differentiating function z with respect to T and equating it to zero,

$$\frac{\partial z}{\partial T} = \frac{0{,}43\,\sigma_{T_{\text{in.}}}\left\{0{,}43\left[1+\left(\frac{T}{T_{\text{lim}}}\right)^2\right]-(D_0+D)\right\}}{T^2\sqrt{1+\left(\frac{T}{T_{\text{lim}}}\right)^2}\,(D_0+D)^2} = 0, \qquad (11)$$

we find the optimum spectrophotometer reading (for which the experimental error is a minimum):

$$D_{\text{expt.}} = 0,43\left[1 + \left(\frac{T_{\text{exp}}}{T_{\text{lim}}}\right)^2\right] - D_0. \tag{12}$$

For $T_{\text{limit}} = \infty$ ($\sigma_{T_{\text{cuvette}}} = 0$), this expression transforms into Hiskey's equation (6).

The optimum reading of the spectrophotometer only depends on the ratio $\frac{\sigma_{T_{\text{inst.}}}}{\sigma_{T_{\text{cuv}}}}$, but does not depend on the absolute values of these errors. The optimum readings in various articles can differ appreciably from each other because of the variability of T_{limit}.

In order to establish the effect of the limiting reading and the optical density of the zero standard on the optimum reading of the spectrophotometer, we differentiate:

$$\frac{\partial T_{\text{expt.}}}{\partial T_{\text{lim.}}} = \frac{2T^3_{\text{expt.}}}{T_{\text{lim}}[T^2_{\text{lim}} + 2T^2_{\text{expt.}}]}, \tag{13}$$

$$\frac{\partial T_{\text{expt.}}}{\partial D_0} = \frac{T_{\text{expt.}} T^2_{\text{lim}}}{0,43\,[T^2_{\text{lim}} + 2T^2_{\text{expt}}]}. \tag{14}$$

Both the derivatives are greater than zero. Accordingly, on increasing T_{limit} and D_0, $T_{\text{expt.}}$ increases ($D_{\text{expt.}}$ decreases), as is evident from Fig. 1.

From equation (12) it follows that for

$$D_0 > 0,43\left[1 + \frac{1}{T^2_{\text{lim}}}\right] \tag{15}$$

$D_{\text{expt.}} \leq 0$, and, accordingly, the maximum experimental accuracy is achieved at $D = 0$, while the minimum error is given by

$$z_{\text{min}} = \frac{0,43\,\sigma_{T_{\text{in.}}}\sqrt{1 + \frac{1}{T^2_{\text{lim}}}}}{D_0} \tag{16}$$

The right part of the inequality (15) has a positive value. Accordingly, $D = 0$ can only be the optimum reading in the differential method. Usually, zero standards with an optical density of D_0 equal to about 2 are used. It can be shown that in this case, condition (15) is fulfilled for $T_{\text{limit}} > 1/2$. However, usually $Y_{\text{limit}} < 1/2$. For example, during determination of titanium as its peroxide complex in sulfuric acid a value of T_{limit} of about $1/4$ was obtained [15]. In Bastian's work [5] T_{limit} was even lower, $1/7.5$. Thus, condition (15) is usually not observed, and, consequently, $D_{\text{expt.}} > 0$. However, as the curve for the accuracy of the differential method shows ($T_{\text{limit}} = 1/4$, Fig.1), the accuracy at $D = 0$ differs little from z_{min}. This means that the range for the optimum readings is wider than Hiskey assumed.

The minimum error is found from equations (10) and (12):

$$z_{\text{min}} = \frac{\sigma_{T_{\text{in}}}}{T_{\text{expt}}\sqrt{1 + \left(\frac{T_{\text{expt}}}{T_{\text{lim}}}\right)^2}}. \tag{17}$$

Formula (17) does not give a clear relationship between the minimum experimental error and the optical density of the zero standard. It was shown above that $T_{expt.}$ increases on increasing D_0. Accordingly, the experimental error $z_{min.}$ is lower, the higher the optical density of the zero standard.

The practical value of the accuracy curves, calculated taking into account T_{limit}, reduces to the fact that they make it possible to choose the range of optical readings more accurately.

The value of 0.43 is given in the literature as the optimum value of the optical density for the absolute method, while it is indicated that the working range for the optical density is approximately 0.2-0.8. This range corresponds to a change in the experimental accuracy of not more than 25% (for σ_T = const.). From equation (12) it follows that in actual fact $D_{expt.}$ is always greater than 0.43 in the absolute method (D = 0).

In Table 1 are given the optimum readings and the working ranges for the optical density scale. In these ranges the experimental accuracy changes by 25%. For the differential method, the optimum readings are given for $D_0 = 1$ and $D_0 = 2$ (in practice this is the limiting value of D_0). The first column in the table ($T_{limit} = 10$) gives the published results (the cuvette error is not taken into account).

As the results given in the table show, the optimum readings are considerably higher than those recommended in the literature.

In the differential method, the working range is several times wider than follows from Hiskey's equation.

It is very important to choose the working range correctly. For example, in the absolute method, for a minimum value of the optical density of the working range recommended in the literature (D = 0.2), the experimental error for $T_{limit} = {}^1/_4$ and $T_{limit} = {}^1/_7$ is 2.3 and 3.1 times the minimum error respectively. Thus, the use of a correct working range leads to a corresponding increase in the accuracy of a determination.

In order to find the optimum reading it is necessary to know T_{limit}, i.e., $\sigma_{T_{inst.}}$ and $\sigma_{T_{cuvette}}$ has been described in the previous communication [15], in which the formula to be used for the calculations were also given.

For speeding up analysis by the absolute method one need not determine $\sigma_{T_{inst.}}$ and $\sigma_{T_{cuvette}}$, but in this case one should use a narrower range of readings of D : 0.6-0.8, since only these readings are included in the working range for all practically possible values of T_{limit} (from 10 to 1/10).

It follows from the curves shown in Fig. 1 that the gain in accuracy of the differential method, as compared with the absolute method, is less than one should expect from the formulas based on the assumption that $\sigma_T =$ = const. [4]. Obviously, it is necessary to compare the minimum errors of each method, and not the errors of the methods for a given test solution as Reilley and Crawford recommend [16].

Calculations show that the increase in accuracy when using a zero standard with an optical density of $D_0 =$ 2, for $T_{limit} = 10$ ($\sigma_{T_{cuvette}}$ about 0) is equal to 12.5, while for $T_{limit} = 1/4$ and $T_{limit} = 1/7$, the values are 4.7 and 3.8 respectively. Accordingly, in order to obtain the highest gain in accuracy, it is necessary to prepare the cuvettes particularly carefully, and to place them in a strictly defined position in order to lower $\sigma_{T_{cuvette}}$.

It is interesting to observe that on spectrophotometers with a high instrumental error $\sigma_{T_{inst.}}$, it is particularly advantageous to use the differential method (T_{limit} is sufficiently large).

The Optimum Concentration of the Zero Standard in the Differential Method

In differential spectrophotometry, as pointed out already, measurements are carried out at large slit widths of the monochromator. As a result, the light beam is not monochromatic and Beer's law is not obeyed. Usually, there is a negative deviation from this law; the slope of the concentration curve u decreases with increasing optical density of the solution (relative to the zero standard) (Fig. 2).

However, the relation between D and c, for a given concentration of the zero standard c_0 remains linear up to a definite value of D and for a sufficiently wide slit of the monochromator. Accordingly, equation (4) still holds, but, in this case, the slope of the straight line u depends on the concentration of the zero standard c_0. Taking $uc_0 = D_0$ as an arbitrary optical density of the zero standard, we obtain equation (7) for the experimental error.

Thus, all the conclusions made already hold true even for the case of a negative deviation from Beer's law. The optimum value of the spectrophotometer is found by means of equation (12). If for $D_{expt.}$ the linear character of the relation between D and c is destroyed, i.e., the slope u decreases, then the measurements should be made at maximum values of D, for which u still remains constant.

Since the experimental error is higher at high values of D_0, the maximum accuracy is achieved for a maximum arbitrary optical density of the zero standard:

$$D_0 = uc_0 = max \qquad (18)$$

TABLE 1

Optimum Readings and the Working Ranges for the Optical Density Scale

Method	T_{limit} \ D_0	10	1	1/2	1/4	1/7	1/10
Absolute	0	0,43 0,20—0,80	0,50 0,25—0,83	0,57 0,31—0,91	0,70 0,42—1,05	0,85 0,53—1,21	1,00 0,63–1,32
Differential	1	0 0—0,15	0 0—0,33	0,20 0—0,55	0,43 0—0,80	0.63 0,13—1,02	0,73 0,24—1,17
	2	0 0—0,12	0 0—0,23	0 0—0,43	0,25 0—0,72	0,50 0—0,95	0,68 0–1,10

TABLE 2

Determination of the Optimum Concentration of the Zero Standard

C_0, mg/ml	Slit width, mm	D	u = D/0.03, ml/mg	uc_0
0,00	0,047	0,456	15,2	0,00
0,03	0,070	0,458	15,2	0.46
0,06	0,113	0,446	14.9	0,90
0,09	0,181	0,428	14,3	1,29
0,12	0,295	0,405	13,5	1,62
0,15	0,468	0,337	11,2	1,68
0,18	0,684	0,262	8,7	1,57

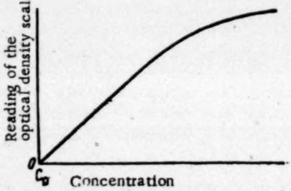

Fig. 2. Negative deviation from Beer's law.

This condition for the choice of the optimum concentration of the zero standard is analogous to the condition found by Hiskey, which was derived for the special case T = const, and $D_{expt.} = 0$.

It should be noted that in order to set the optical density scale on zero for each new zero standard, it is only necessary to change the slit width of the monochromator, and not to change the sensitivity by means of the potentiometer: otherwise $\sigma_{T_{inst.}}$ will increase and condition (18) will not be valid (see equation 10).

In Table 2 are given the results for determination of the optimum concentration of the zero standard for the analysis of titanium by means of H_2O_2. The method suggested by Bastian was used [5]. A series of solutions of titanium in 20% H_2SO_4 with concentrations ranging from 0 to 0.21 mg/ml at intervals of 0.03 mg/ml, was prepared. Hydrogen peroxide was added to the solutions. Each solution was measured photometrically with respect to the previous solution which had a lower concentration (0.03 mg/ml less). Measurements were made on a SF-4 spectrophotometer using a cuvette with a layer thickness of 1 cm. The sensitivity of the spectrophotometer was $s = 2$ divisions of the milliammeter per percent transmission; the wavelength of 408 mμ corresponded to the maximum of the absorption spectrum of the peroxide complex of titanium.

The highest arbitrary optical density was found for a concentration of the zero standard of 0.15 mg/ml. However, the slit width for this concentration was 1.5 times greater than that for 0.12 mg/ml, for only an insignificant gain in accuracy. Accordingly, we took 0.12 mg/ml as the optimum concentration.

SUMMARY

A brief review is given of the equations for precision in spectrophotometric determinations.

Optimum conditions for spectrophotometric determinations are carried out taking into account the non-reproducibility of the state of the cuvette. It is shown that the optimum readings on the optical density scale published in the literature are considerably too low. The working range of the scale readings in the differential method is considerably wider than that calculated without taking into account the cuvette error.

The Bastian-Hiskey condition for choosing the optimum concentration of the zero standard is still valid when the non-reproducibility of the state of the cuvette is taken into account.

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THE ANALYTICAL APPLICATION OF 8-MERCAPTOQUINOLINE (THIOOXINE) AND ITS DERIVATIVES

COMMUNICATION 7. INNER COMPLEX SALTS OF THE HALOGEN DERIVATIVES OF 8-MERCAPTOQUINOLINE AND THEIR SOLUBILITY IN ORGANIC SOLVENTS*

Yu. A. Bankovskii and E. F. Lobanova

For increasing the sensitivity of the determination of low concentrations of elements by photometric and other methods, extraction of such elements from a large volume of aqueous phase into a small volume of organic solvent is often carried out. The possibility of extracting individual components of a complex mixture from one phase into another is important, not only for colorimetry , but also as a preliminary operation in other methods of chemical analysis and in technology. In connection with enrichment of the extraction it is of interest to study the relation between the solubility of the inner complex salts of the metals and the structure of the reagent molecule, and to study the nature and position of substitutents in derivatives of the reagent. The solubility of the inner complex salts of 8-hydroxyquinoline in organic solvents has been studied most fully. It has been established that most of the inner complex salts of 8-hydroxyquinoline (in particular,in the anhydrous state) are soluble in certain organic solvents [1-5]. The solubility of the inner complex salts of the halogen derivatives of 8-hydroxyquinoline has also been studied. The opinion has been expressed that "Multihalogen substituted and dihalogen substituted derivatives, as a rule, are the most readily extracted by all types of solvents" [6]. Actually, the inner complex salts of 5- and 7-halogen substituted 8-hydroxyquinoline dissolve more readily in organic solvents than the salts of 8-hydroxyquinoline. This is explained by the fact that the halogens in the 5- and 7-positions considerably enhance the acidic properties of the hydroxyl group of 8-hydroxyquinoline. All the same one cannot fully agree with this statement, since a halogen atom in the 2-, 4-, and also in the 6-position, while decreasing the basic properties of nitrogen of the pyridine ring of 8-hydroxyquinoline, will presumably exhibit a negative influence on the solubility of the inner complex salts in organic solvents. This is confirmed by a study of the extractability of the inner complex salts of 8-mercaptoquinoline and its halogen derivates.

As our experiments have shown, 8-mercaptoquinoline forms with many metals intensely colored inner complex salts which are readily soluble in many organic solvents. The salts of 8-mercaptoquinoline proved to be considerably more stable in all cases than the corresponding salts of 8-hydroxyquinoline [7].

The present article contains results of a study of the effect of the position of the halogen atom in the reagent molecule on the analytical properties of 8-mercaptoquinoline, and on the properties of its inner complex salt. A study was made of the interaction of 3-bromo-8-mercaptoquinoline (II), 5-bromo-8-mercaptoquinoline (III), and 6-bromo-8-mercaptoquinoline (IV), with metals, forming sulfides which are stable to the action of water, and a comparison was made of the extractability of the inner complex slats of the reagents mentioned with the extractability of the salts of 8-mercaptoquinoline (I).

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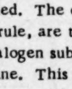

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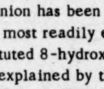

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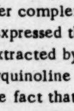

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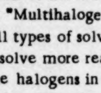

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*For Communication 6, see Bull. Acad. Sci. Latvian SSR No.3, 121 (1958).

The Solubility of the Inner Complex Salts of 8-Mercaptoquinoline (Thiooxine) and its Derivatives in Organic Solvents*

Cation and medium	I 8-Mercaptoquinoline					II 3-Bromo-8-mercaptoquinoline					III 3-Bromo-8-mercaptoquinoline					IV 6-Bromo-8-mercaptoquinoline				
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
	CCl_4	C_6H_6	$CHCl_3$	$C_5H_{11}OH$	$(C_2H_5)_2O$	CCl_4	C_6H_6	$CHCl_3$	$C_5H_{11}OH$	$(C_2H_5)_2O$	CCl_4	C_6H_6	$CHCl_3$	$C_5H_{11}OH$	$(C_2H_5)_2O$	CCl_4	C_6H_6	$CHCl_3$	$C_5H_{11}OH$	$(C_2H_5)_2O$
Fe^{2+} acid, neutral, alkaline	Red-brown					Cherry-red					Cherry-red					Red-brown				
	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
Ni^{2+} weakly acid, neutral, alkaline	Raspberry					Cherry					Cherry					Cherry-red				
	+++	++	+++	++	++	++	+++	+++	+++	++	+++	+++	+++	+++	+++	+	++	++	++	+
Co^{2+} weakly acid, neutral, alkaline	Brown					Cherry					Red-brown					Cherry-red				
	+++	+++	+++	++	++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	++	+++	+++	+++	++
Pd^{2+} acid, neutral, alkaline	Rose-red					Raspberry					Raspberry					Red				
	++	+++	+++	+++	+++	++	+++	+++	+++	+++	+++	+++	+++	+++	+++	++	++	+++	+++	++
Mo^{IV}** acid	Yellow-green					Yellow					Yellow					Yellow				
	++	+++	+++	+++	++	++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+	+++	+++	+++	++
Cu^{2+} acid, neutral, alkaline	Brown-yellow					Cherry-brown					Red-brown					Cherry-red				

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*The following scheme has been adopted for designating the solubility: O – insoluble; + very sparingly soluble; ++ average solubility; +++ readily soluble; - does not react.

**In alkaline medium does not interact with 8-mercaptoquinoline and its derivatives.

TABLE (Cont'd).

Cation and medium	8-Mercaptoquinoline					3-Bromo-8-mercaptoquinoline					5-Bromo-8-mercaptoquinoline					6-Bromo-8-mercaptoquinoline				
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
	CCl_4	C_6H_6	$CHCl_3$	$C_5H_{11}OH$	$(C_2H_5)_2O$	CCl_4	C_6H_6	$CHCl_3$	$C_5H_{11}OH$	$(C_2H_5)_2O$	CCl_4	C_6H_6	$CHCl_3$	$C_5H_{11}OH$	$(C_2H_5)_2O$	CCl_4	C_6H_6	$CHCl_3$	$C_5H_{11}OH$	$(C_2H_5)_2O$
Pb^{2+} weakly acid, neutral alkaline	Yellow					Yellow					Yellow					Yellow				
	+++	++	+++	+	+	++	++	++	+++	+++	+++	+++	+++	+++	+++	+	+	++	+	+
Pt^{4+} ** acid, neutral	Raspberry					Blue-violet					Blue-violet					Violet-rose				
	+++	+++	+++	+++	+	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	++	++	+++	+++	++
Ag^+ acid, alkaline	Yellow in alkaline and red in acid media					Yellow in alkaline and red in acid media					Yellow in alkaline and red in acid media					Yellow in alkaline and red in acid media				
	0 0	0 0	0 0	0 0	0 0	+ 0	+ 0	++ +	++ +	0 0	+++ +	+++ +	+++ +	+++ +	+++ +	0 0	0 0	0 0	0 0	0 0
Tl^+ neutral or alkaline	Bright-yellow					Bright-yellow					Bright-yellow					Bright-yellow				
	+++	+++	+++	+++	++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
Os^{VIII} acid, neutral	Blue					Bluish					Blue-violet					Bluish-brown				
	++	++	+++	+++	++	++	++	+++	+++	++	++	+++	+++	+++	++	+	++	+++	++	++
In^{3+} acid, neutral, alkaline	Yellow					Yellow					Yellow					Yellow				
	+++	+++	+++	+++	+++	+++	+++	+++	+++	++	+++	+++	+++	+++	+++	++	+++	+++	+++	++

TABLE (Cont'd).

$V^{V\bullet\bullet}$ weakly acid	Green					Green					Green									
	+++	+++	+++	+++	+++	++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
Mn^{2+} weakly acid, neutral, alkaline	Brown					Brown					Brown					Brown				
	− ++	− +++	− +++	− +++	− ++	++ ++	+++ +++	+++ +++	+++ +++	++ ++	+++ +++	+++ +++	+++ +++	+++ +++	+++ +++	− ++	− ++	− +++	− +++	− +
Zn^{2+} acid, neutral, ammoniacal	Yellow					Yellow					Yellow					Yellow				
	+	+++	+++	++	++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	+	+	++	++	+
Ir^{3+} acid, neutral, alkaline	Brown					Cherry-brown					Brown					Yellow-brown				
	+++ + −	+++ + −	+++ ++ −	+++ + −	+++ + −	+++ +++ +	+++ +++ +	++ +++ ++	+++ +++ +	+++ +++ +	+++ +++ +	+++ +++ +	+++ +++ ++	+++ +++ ++	+++ +++ +	+++ 0 −	+++ + −	+++ + −	+++ + −	+++ 0 −
Hg^{2+} acid, neutral, alkaline	Bright-yellow					Bright-yellow					Yellow					Bright-yellow				
	0	0	+	+	0	+	+	++	+	+	+++	+++	+++	+++	+++	0	0	+	+	0
$W^{VI\bullet\bullet}$ acid	Very bright yellow					Yellow					Greenish-yellow					Green precipitate				
	0	0	+	+++	0	++	++	+++	+++	+	+++	+++	+++	+++	+++	0	0	0	0	0
Sb^{3+} acid, neutral	Yellow					Yellow					Yellow					Yellow				
	+	+++	+++	+++	+++	+	++	+++	+++	++	+++	+++	+++	+++	+++	+	+	+++	+++	0
Bi^{3+} acid, neutral, alkaline	Yellow					Yellow					Yellow					Yellow				
	0	+	+++	+++	+	++	++	+++	+++	++	++	+++	+++	+++	++	+	+	++	++	+
Cd^{2+} acid, neutral, ammoniacal	Yellow					Yellow-orange					Yellow-orange					Yellow-orange				
	0	0	++	+	0	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++	0	0	+	+	0

Of the halogen derivatives of 8-mercaptoquinoline only 5-bromo-8-mercaptoquinoline [8] and 4-chloro-8-mercaptoquinoline [10] have been described in the literature. We synthesized 3-bromo-8-mercaptoquinoline and 6-bromo-8-mercaptoquinoline by a method similar to the method for preparing 8-mercaptoquinoline [8,9].

8-Mercaptoquinoline and its derivatives, like all reagents containing the mercapto group, possess reducing properties, as a result of which the higher valence states of elements possessing oxidizing properties, e. g., Fe^{III}, Cu^{II}, Pt^{IV}, Au^{III}, Os^{VIII}, Ir^{IV} are reduced to the lower valence states which interact with excess reagent. The reagent is thereby itself oxidized to the disulfide.

During a study of the interaction of the halogen derivatives of 8-mercaptoquinoline mentioned with the elements, 5% alcoholic solutions or aqueous-alcoholic solutions of the reagents were used.

To some milliliters of an aqueous solution of the metal (about 0.1 mg) contained in a test tube, and with a definite pH, was added 2-3 ml of a 5% solution of reagent (excess), and the precipitate of the inner complex salt which separated out was extracted (by intense shaking with 3 ml of solvent) and its solubility tested in the various organic solvents immiscible with water.

The results of these experiments are given in the table.

It is clear from the results in the table that the solubility in the organic solvents of the compounds formed between cations in the hydrogen sulfide and ammonium sulfide groups with the bromo derivatives of 8-mercaptoquinoline depends to a considerable extent on the position of the halogen atom in the reagent molecule. The most soluble salts are those of 5-bromo-8-mercaptoquinoline, which testifies, apparently, to the fact that the increase in the acid properties of the mercapto group (thanks to the para position of the bromine atom with respect to —SH) increases the intermolecular dissociation of the inner complex salt, and facilitates the coordination interaction of the metal atom with the nitrogen of the heterocyclic ring of the quinoline. A similar effect on the mercapto group is shown by the bromine atom in the third position in the molecule of 8-mercaptoquinoline; this apparently explains the increase in the solubility of 3-bromo-8-mercaptoquinolates as compared with 8-mercaptoquinolates. Bromine in the sixth position, by decreasing the basic properties of the nitrogen, and making coordination of the metal with nitrogen more difficult, leads to a decrease in the solubility of the 6-bromo-8-mercaptoquinolates as compared with the 8-mercaptoquinolates. This could be confirmed by studying the solubility of the inner complex salts of 4-chloro-8-mercaptoquinoline, whose synthessis had been worked out [10].

The table also shows that the inner complex salts of 8-mercaptoquinoline and its halogen derivatives exhibit the highest solubility in polar solvents (chloroform, isoamyl alcohol); their solubility is considerably less in non-polar solvents (benzene, carbon tetrachloride).

SUMMARY

The solubility in organic solvents of the inner complex salts of the halogen derivatives of 8-mercaptoquinoline depends on the position of the halogen in the reagent molecule. Compared with the solubility of the salts of 8-mercaptoquinoline, the salts of its 3- and 5-halogen derivatives possess considerably better solubility. Location of the halogen in the sixth position leads to a considerable decrease in the solubility of the inner complex salts in organic solvents. The solubility of the inner complex salts of 8-mercaptoquinoline and its halogen derivatives is highest in strongly polar solvents.

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THE USE OF TETRAETHYLAMMONIUM HYDROXIDE FOR THE POTENTIOMETRIC TITRATION OF WEAK ACIDS IN NON-AQUEOUS SOLUTIONS

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Methods of titrating in non-aqueous solutions have acquired great importance in recent years [1]. The rapid development of methods of non-aqueous titration is explained by their many advantages. It is sufficient to point out that only by means of the method of acid–base titration in a suitable non-aqueous medium is it possible to determine acids and bases, independently of their pH, primary, secondary, and tertiary amines, amino acids, phenols, aminophenols, nitro compounds, enols, imides, anhydrides, and chloroanhydrides, the salts of organic and inorganic acids, alkaloids, vitamins, and many other compounds. Moreover, in non-aqueous media, it is possible to carry out differential titration of various mixtures of strong and weak acids, and mixtures of bases, independently of their organic and inorganic nature and character, and to titrate differentially the salts of weak acids in the presence of free bases, elementalorganic compounds in general, and organosilicon compounds in particular, etc. [2-5]

Of particular interest is titration in non-aqueous media of weak and very weak monobasic and multibasic acids and their mixtures, which cannot be titrated in aqueous media.

In 1948 Moss, Elliot, and Hall [6] successfully used the method of potentiometric titration of weak acids in ethylenediamine. They used a solution of sodium aminoethylate in the same solvent as titrant. Japanese authors [7, 8] have titrated phenols and other weak acids, using the hydrides and amides of lithium and aluminum. More recently, Fritz and other scientists [9-11] used lithium, sodium, and potassium methylates in a benzene-methanol medium for titrating weak acids, and also sodium triphenylmethane in a benzene-ether medium.

Research has shown that the use of the alcoholates of the alkali metals as titrants for the determination of acidic materials suffers from a number of drawbacks. Solutions of the alcoholates are not stable enough, while during titration of certain organic acids by means of these alcoholates, precipitates are formed which interfere with potentiometric titration.

Deal and Wyld [12] used as titrant a solution of potassium hydroxide in isopropanol, but, even in this case, during titration of organic acids precipitates often form. Moreover, in the presence of K^+ and Na^+ the glass electrode loses its sensitivity. Accordingly, they used tetrabutylammonium hydroxide in aqueous isopropanol for titrating weak acids. The tetrabutylammonium salts of weak acids dissolve more readily in organic solvents than the corresponding potassium and sodium salts. Deal and Wyld titrated weak acids with a glass electrode. The latter did not lose its sensitivity in the presence of quaternary ammonium base ions; accordingly, good titration curves were obtained.

Harlow, Noble, and Wyld [13] continued the work on titration of weak acids with tetrabutylammonium hydroxide in absolute isopropanol. Cundiff and Markunas [14] prepared a solution of tetrabutylammonium hydroxide using a mixture of benzene and methanol. Firtz and Yamamura [15] used a solution of triethyl-n-butylammonium hydroxide in a mixture of benzene and methanol as titrant for the potentiometric determination of weak acids in an acetone medium. Other research workers have also used tetrabutylammonium and triethyl-n-butylammonium hydroxides for titrating mixtures of acids. [16-18]. Ethylenediamine, pyridine, dimethylformamide, n-butyalamine, acetone, methyl ethyl ketone, methyl isobutyl ketone, acetonitrile, isopropanol, etc. have also been used as solvents for this same purpose [2,12-14,16].

Harlow et al [13] have noted that tetrabutylammonium hydroxide is not the best organic base for titrating weak acids in non-aqueous solutions. The authors suggest that more convenient and less expensive methods of preparing the basic titrants might be developed in the future.

Over a period of years we have studied methods of titrating the most diverse materials in non-aqueous solutions. We have repeated, checked, improved, and critically evaluated numerous methods suggested in the Russian and foreign literature, and have also developed new methods for titrating in organic solvent media.

The present article is devoted to the description of a new method which we have developed for titrating weak and very weak acids in non-aqueous solutions by means of tetraethylammonium hydroxide.

We have tested the methylates, ethylates, and hydroxides of the alkali metals, and also organic and other bases as titrants. Tetraethylammonium hydroxide, which is readily available, has proved in many respects to be better than any of the basic titrants used hitherto for the titration of weak and very weak acids. Commercial tetraethylammonium iodide can be used for preparing it; it forms readily soluble salts with organic acids. Good titration curves with sharp breaks are obtained on using a glass electrode in various solvents. Tetraethylammonium hydroxide can also be used very succesfully for titrating by means of an indicator method.

EXPERIMENTAL

Preparation of the titrant. Tetraethylammonium iodide is recrystallized from absolute alcohol. Tetraethylammonium hydroxide is prepared from the iodide by means of the following reaction:

$$(C_2H_5)_4NI + AgOH \rightarrow (C_2H_5)_4NOH + AgI$$

For this purpose, 30 g of tetraethylammonium iodide dried in air is dissolved in 300 ml of absolute methanol and shaken for an hour and a half with 30 g of finely ground silver oxide. The mixture is filtered and diluted to 1 liter with dry benzene. The tetraethylammonium hydroxide solution is standardized by titrating it with aliquots of chemically pure benzoic acid. The methanol-benzene solution of $(C_2H_5)_4NOH$ is fairly stable and does not change on storing for a long time. Thus, in the course of two months the normality of the tetraethylammonium hydroxide solution changed from 0.1022 to 0.1013.

Choice of solvent. The following solvents were tested as potential media for titration: methyl, ethyl, butyl, isobutyl, propyl, and isopropyl alcohols; n-butylamine, ethylenediamine, triethylamine, hydroxylamine; formamide, acetamide, dimethylformamide; acetone, methyl ethyl ketone, methyl butyl ketone, methyl isobutyl ketone; acetonitrile, pyridine, and other solvents, and also mixtures of these solvents. The best solvent proved to be methyl ethyl ketone, which possesses a number of valuable properties, and is a good solvent for a large number of materials. In this medium it is possible to titrate weak acids and to titrate mixtures of acids differentially.

Titration method. Weak acids were titrated potentiometrically in the usual setup. The latter consisted of a 10 ml semimicro buret graduated in 0.02 ml, a titration beaker into which the glass and calomel electrodes were lowered, a potentiometer, a magnetic stirrer, and a system for drying nitrogen. Titration was carried out in a stream of nitrogen which was dried by passing it through a calcium chloride tube. The top end of the buret was also closed with a calcium chloride tube. Potentials were measured with a LP-5 potentiometer. So that no water diffused into the system during titration, the saturated solution of KCl in water was replaced by a saturated solution of KCl in methanol. This makes it possible to get a large potential jump.

30 ml of methyl ethyl ketone was poured into the titration beaker followed by 2-3 drops of thymol blue indicator (a 0.3% solution in methanol); a weak stream of nitrogen was passed through the system and the titrant added to the appearance of a blue color of the indicator in order to neutralize acid impurities present in the original solvent. 0.02-0.05 g of test material was weighed out on an analytical balance and transferred into the titration beaker, and the whole stirred with the magnetic stirrer. The titrant was added in 0.1 ml aliquots until the equivalence potential was obtained, when it was added in 0.05 ml aliquots. Titration was continued until the potential had reached a maximum and remained relatively constant on addition of more titrant. The

potentiometric titration curve was then plotted within the coordinates ml – millivolts, and the equivalence point established. Calculations were made as usual by subtracting the volume of titrant used for neutralizing the acid impurities in the solvent from the total amount of titrant used (usually, this correction amounts to 0.1 ml).

Before each titration the normality of the tetraethylammonium hydroxide solution was checked against chemically pure benzoic acid, either potentiometrically or visually, using thymol blue. When titrations were carried out at temperatures different to that at which the solution was standardized, a correction of 1 ± (t × 0.001) was applied, where t is the difference between the temperatures in °C at which the solution was standardized and the determination carried out.

Titration Results. Using tetraethylammonium hydroxide dissolved in various solvents, we titrated a large number of organic and inorganic acids. We titrated mono-, di-, and tribasic carboxylic acids; formic, acetic, propionic adipic, anthranilic, oxalic, succinic, maleic, glutaric, tartaric, malic, camphoric, fumaric, benzoic, salicylic, and phthalic acids, etc., and also their mixtures. In addition, we also titrated such weak acids as phenols, and also their mixtures with carboxylic acids. Of the inorganic acids, we used for this purpose hydrochloric, nitric, perchloric, and sulfuric acids, and mixtures of these acids with organic acids.

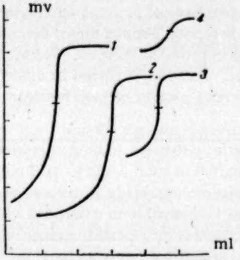

Fig. 1. Titration of weak and very weak acids in a medium of methyl ethyl ketone: 1) Formic; 2) salicylic; 3) benzoic; 4) phenol.

In Fig. 1 are shown titration curves of weak organic acids: formic ($K = 1.8 \cdot 10^{-4}$), salicylic ($K = 1.06 \cdot 10^{-3}$), benzoic ($K = 6.3 \cdot \cdot 10^{-5}$), and phenol ($K = 1.3 \cdot 10^{-10}$). As is evident, tetraethylammonium hydroxide is a sufficiently strong base for titrating even such a weak acid as phenol in a medium of methyl ethyl ketone.

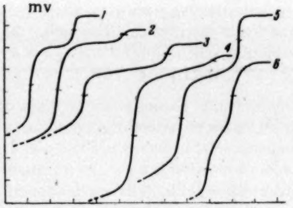

Fig. 2. Titration of dibasic acids in a medium of methyl ethyl ketone: 1) Malic; 2) malonic; 3) succinic; 4) phthalic; 5) oxalic; 6) maleic.

Titration curves for dibasic acids are shown in Fig. 2. During titration of malic ($K_1 = 4 \cdot 10^{-4}$ $K_2 = 6 \cdot 10^{-6}$) malonic ($K_1 = 1.71 \cdot 10^{-3}$; $K_2 = 2.0 \cdot 10^{-6}$), succinic ($K_1 = 6.9 \cdot 10^{-5}$; $K_2 = 2.5 \cdot 10^{-6}$), maleic ($K_1 = 1.17 \cdot 10^{-2}$; $K_2 = 2.6 \cdot 10^{-7}$), phthalic ($K_1 = 1.3 \cdot 10^{-3}$; $K_2 = 3.9 \cdot 10^{-6}$) and oxalic ($K_1 = 5.9 \cdot \cdot 10^{-2}$; $K_2 = 6.4 \cdot 10^{-5}$ acids, two potential jumps are observed on each titration curve. Of particular interest is the titration curve for succinic acid on which is observed two clearly defined jumps. In this case the dissociation constants of this acid in water are very close to each other ($K_1 = 6.9 \cdot 10^{-5}$ and $K_2 = 2.5 \cdot 10^{-6}$).

During titration of the tribasic acid citric acid ($K_1 = 8.4 \cdot \cdot 10^{-4}$, $K_2 = 1.8 \cdot 10^{-5}$ and $K_3 = 4 \cdot 10^{-6}$) a curve with three potential jumps was obtained (Fig. 3).

Results of titrating mixtures of acids are shown in Fig. 4. During titration of a mixture of malic and benzoic acids, three breaks were obtained on the curve. The dissociation constants of malic acid in water are $K_1 = 4 \cdot \cdot 10^{-4}$ and $K_2 = 6 \cdot 10^{-6}$, while the dissociation constant of benzoic acid is $K_1 = 6.3 \cdot 10^{-5}$. On this curve, the first and third breaks correspond to the two acid equivalents of malic acid, while the second break corresponds to the equivalent of benzoic acid. In Fig. 2 the first and third potential jumps correspond to the first and second stages of neutralization of malonic acid (dissociation constants $K_1 = 1.7 \cdot 10^{-3}$ and $K_2 = 2.7 \cdot 10^{-6}$), while the second jump corresponds to the neutralization of benzoic acid ($K = 6.3 \cdot 10^{-5}$). In Fig. 3 are seen four potential jumps (mixture of oxalic and malic acids). The first and third breaks corresponds to oxalic acid, while the second and fourth breaks correspond to malic acid. Results for the titration of a mixture of phenol with benzoic acid and oxalic acid are given in Curves 4 and 5.

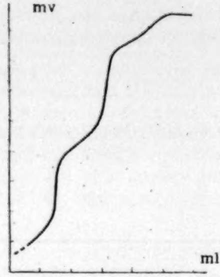

Fig. 3. Titration of citric acid in a methyl ethyl ketone medium.

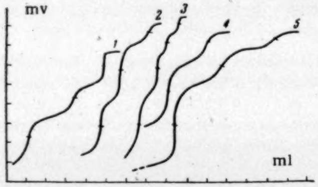

Fig. 4. Titration of mixtures of organic bases in a methyl ethyl ketone medium. 1) Malic + benzoic; 2) malonic + benzoic; 3) oxalic + malic; 4) benzoic + phenol; 5) oxalic + phenol.

DISCUSSION OF ANALYTICAL RESULTS

It is impossible to titrate weak acids such as phenol ($K = 10^{-10}$) directly, since it is impossible to determine the end point. Research has shown that tetraethylammonium hydroxide in a mixture of benzene and methanol is a sufficiently strong base, and permits direct determination of very weak acids even in non-aqueous media. Thus, during the potentiometric titration of phenol in methyl ethyl ketone, a curve with a clearly defined break is obtained.

Titration in water of polybasic acids or mixtures of acids leads to determination of total acidity. It is only in cases where the dissociation constants of the two acids differ by 10^4 times, that it is possible to determine them differentially in their mixtures by a potentiometric method. During titration with tetraethylammonium hydroxide in organic solvents, it is possible to determine each stage of electrolytic dissociation of such acids as oxalic, malic, and malonic acids whose dissociation constants for the first and second stages differ by 10^2 - 10^3 times. Of particular interest is the titration curve for succinic acid which exhibits two breaks, the dissociation constants of this acid being $K_1 = 6.9 \cdot 10^{-4}$ and $K_2 = = 2.5 \cdot 10^{-5}$, i.e., they differ by only ten times each other. A clearly defined curve with three jumps is obtained during titration of the tribasic citric acid, the dissociation constants of which in water are $K_1 = 8.4 \cdot \cdot 10^{-4}$, $K_2 = 1.8 \cdot 10^{-5}$, and $K_3 = 4 \cdot 10^{-6}$.

It is possible to titrate phenol in the presence of carboxylic acids by means of tetraethylammonium hydroxide. The experimental accuracy is about 1%. Thus, tetraethylammonium hydroxide is a good basic titrant for the determination of weak acids. The application of such solvents as methyl ethyl ketone makes it possible to carry out differential titration of mixtures of acids.

Titration with tetraethylammonium hydroxide in non-aqueous solutions of strong, weak, and very weak acids, and of their mixtures should find wide application in analytical chemistry.

SUMMARY

A study has been made of the titration of strong, weak, and very weak acids, and of their mixtures, in non-aqueous media by means of a solution of tetraethylammonium hydroxide in benzene-methanol. Tetraethylammonium hydroxide is a strong alkaline titrant which permits the determination not only of strong and weak (carboxylic) acids, but also of very weak acids (phenol). Mixtures of strong, weak, and very weak acids can be titrated in non-aqueous media by means of tetraethylammonium hydroxide. Titration with tetraethylammonium hydroxide in methyl ethyl ketone can be carried out either visually or potentiometrically; the curves obtained thereby are characterized by sharp potential jumps.

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A LOW TEMPERATURE CARBON ARC AS A SPECTRUM EXCITATION SOURCE FOR RUBIDIUM , CESIUM, THALLIUM, AND INDIUM DURING SPECTROGRAPHIC ANALYSIS OF SILICATES

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In addition to the acetylene-air flame which is widely used for the quantitative spectrographic determination of small amounts of Rb, Cs, In, and Tl in solutions, of interest is their more rapid direct determination in powdered materials. The most suitable excitation source in this case is a d.c. arc; such an arc ensures rapid passage of the test materials into the gas cloud, while giving the possibility of creating "moderate" temperature conditions of excitation. This favors determination of elements with low ionization potentials, the sensitive lines of which belong to the spectra of non-ionized atoms.

Below is considered certain features of a d.c. carbon arc operating under conditions which ensure determination of Rb, Cs, Tl, and In present as impurities in silicate rocks; conditions are outlined for their quantitative spectrographic determination.

Characteristics of the Determination of Rb, Cs, Tl, and In in a Carbon Arc During the Analysis of Silicates, and the Choice of Spectrum Excitation Conditions

Rubidium, cesium, thallium, and, to a lesser extent, indium [1] pass from the electrode canal into the arc flame at the beginning of arc burning, together with potassium and sodium which are usually present in natural silicates. The low temperature of a silicate melt containing alkali metals favors separate evaporation of elements differing from each other in volatility; this means that when the spectrum of the arc flame is photographed during evaporation of potassium and sodium, it is possible to reduce the superposition of the lines of less volatile elements, which pass into the arc plasma later, on the lines of rubidium, cesium, thallium, and indium.

The order in which the lines of the elements appear in the flame of a low temperature arc during the evaporation of silicates with a high potassium content from an anode in the shape of a wine glass, is characterized by the following volatility series:

[(Tl, Cd, Bi, Pb, Cs, Rb, Na), In, Sn, Ge, Ag, Cu, Mo, Li]*
Ga, Ni, Fe, Mn, Cr, Co, V, Si, Al, Mg, Ca, Nb, Sr, Be,
W, Ib, It, Ti, Ba, La, Zr, Th.

This series is similar to the volatility series found earlier for elements during evaporation of oxide ores.

The order in which rubidium and cesium pass into the arc plasma is wholly determined by the time taken for the other alkali elements (in this case—dominating amounts of potassium) to pass into the plasma. Thallium evaporates more rapidly than the alkali metals (in the first 15-20 seconds of arc burning); indium passes into the flame from the beginning of arc burning right up to complete evaporation of potassium, and approximates to lithium with respect to its volatility. The effect of fractional, separate, passage of elements into the arc flame becomes more and more pronounced as one goes along from the beginning of the volatility series to its middle; elements which are located far enough from sodium and potassium, in practice, pass into the arc flame only after complete evaporation of the alkali metals from the drop of molten silicate.

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*The elements in the square brackets are those elements which pass into the arc cloud during evaporation of potassium present in excess amounts.

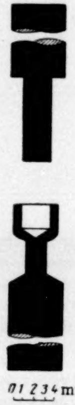

Fig. 1. Electrodes for determination of rubidium, cesium, thallium, and indium in silicates.

When sufficiently large amounts of potassium and sodium which possess the lowest ionization potentials (K = 4.34 electron volt; Na = 5.12 electron volt) are present, the temperature of the arc flame initially drops (approximately to 4000°), and then, as the melt becomes free from potassium and sodium, it rises fairly rapidly to 5000-6000° [2].

The drop in temperature of the arc when potassium and sodium are passing into the flame creates conditions for determination of small amounts of rubidium, cesium, and indium on the basis of their violet lines, and thallium on the basis of its ultraviolet lines, located in the region of the cyanide band, which is sharply weakened on lowering the arc temperature [3,4].

The lines Rb I 4201.85 and Rb I 4215.56, Cs I 4555.36 and Cs I 4593.18, Tl I 3775.72 and In 4101.77 and In 4511.32 are located comparatively near to each other when spectrographs with a dispersion of 6-8 A/mm are used. This makes it possible to carry out a simultaneous determination of the elements listed by photographing the spectrum of one aliquot of material. Rubidium and cesium can also be determined on the basis of their more intense and sensitive infrared lines: Rb I 7800.23 and Rb I 7949.60, Cs I 8521.10 and Cs I 8943.50 [5], which appear in the spectra of silicates for rubidium and cesium contents of the order of $n \cdot 10^{-4}$%.

The main difficulty in the quantitative determination of rubidium, cesium, thallium, and indium in silicates is the variation in the composition of the test samples, in particular the variation in their potassium and sodium contents. The variation in the amounts of sodium and potassium in the silicate melt not only influences the temperature conditions for exciting the elements in the arc flame, but also the conditions of the passage of the other elements into the arc cloud. Moreover, the kinetics of the evaporation of the elements is reflected in the distribution of the concentrations of the elements in the flame, and in the line intensity of the test elements. From this there arise systematic errors in evaluating the concentration of the test elements in the silicates [6,7]. Accordingly, rubidium, cesium, thallium, and indium can only be determined successfully in silicates and other materials of variable composition by carrying out the determination under standard conditions for the passage of the test elements together with potassium and sodium into the arc flame. As our observations have shown, the best conditions are attained on evaporating mixtures of the test silicate with excess potassium sulfate from an electrode crater which ensures a high rate of passage of the alkali metals and also of the alkali metals and also of thallium and indium into the arc cloud. The high rate of evaporation of the elements increases their concentration in the zone of the arc flame lying close to the electrode from which the test sample is being evaporated, and increases the line intensity, and, accordingly, the sensitivity of the determination of the elements.

The form chosen for the anode (Fig. 1) ensures the necessary heating of the cup containing the test material using a low current, and favors a more rapid and uniform evaporation of the volatile compounds of the elements and potassium from the silicate melt formed in it; under such conditions, a significant improvement in the reproducibility of the determinations is observed. The electrode cup is bored out by means of a special cutting tool and has an internal diameter of 3.6 mm, a depth of 3 mm, and walls with a thickness of 0.7 mm. A collar 2.2-2.5 mm in diameter and 4 mm long is turned with a chisel underneath the cup. The cylindrical end of the upper carbon electrode (cathode), with a diameter of 3 mm is set up at a distance of 5 mm from the cup anode.

It should be remembered that the temperature conditions of excitation in the arc cloud can only be kept constant in the presence of a large amount of potassium in the powdered test silicate. Only under such conditions is there created a sufficiently high concentration of potassium in the arc flame. From an examination of Fig. 2 e.g., it is evident that with increasing potassium sulfate content in the silicate powder up to 40-50%, the difference in potential across the electrode faces drops continuously; consequently [1,6,8] the temperature of the arc flame also drops; when more than 50% potassium sulfate is present the temperature becomes almost constant.

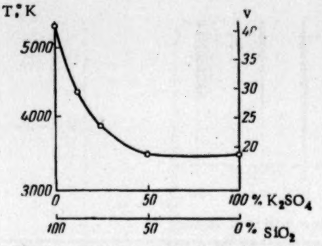

Fig. 2. Relation between the temperatures of a d.c. carbon arc and the potential difference across the electrode faces as a function of the K_2SO_4 content of the quartz being evaporated.

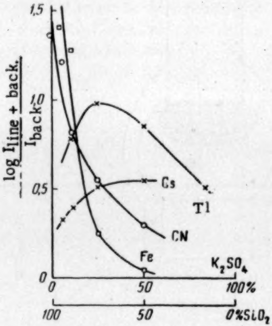

Fig. 3. The effect of the percentage content of K_2SO_4 in the silicate being evaporated on the relative intensity of test lines and background when the central part of the arc flame is photographed — Cs 4555.3 A; Tl 3775.72 A Fe I 4307.9 A; CN in the region 4200 A.

The drop in temperature of the arc flame caused by addition of K_2SO_4 to the silicate powder is accompanied in the course of the first two minutes of arc burning by a sharp attenuation of the intensity of the cyanide bands, which interfere with the determination of rubidium, cesium, thallium, and indium; this attenuation of the cyanide band naturally favors an increase in the intensity of the lines of the test elements (in particular the lines of cesium and rubidium). This is clear from Fig. 3, which illustrates the relation between the intensity of one of the cyanide bands in the region 4200 A, and also of the cesium line, and the concentration of potassium sulfate in the silicate being evaporated in the arc; for the thallium lines there is observed a maximum intensity for a content of 25-30% of K_2SO_4 in the silicate. It should, however, be pointed out that in order to extinguish the cyanide bands satisfactorily, a higher K_2SO_4 concentration is necessary. The weakening of the intensity of the spectral lines of iron, one of which Fe I 4202.03 A is partially superimposed on the line Rb I 4201.85, is caused to a significant extent by the decrease in the evaporation of iron from the melt on increasing the potassium sulfate content of the melt. This can also explain the weakening observed in the spectra of Ti, Ni, and other less volatile elements. The part played by potassium sulfate is particularly clearly manifested for that part of the arc flame lying close to the cup of the lower electrode, from which potassium vapors evaporate intensively into the discharge; this region occupies a large part of the discharge flame. On going from the lower electrode (anode) to the upper (cathode) electrode there is initially observed a slow, and then a sharp increase in the intensity of the cyanide bands in the region of the arc directly adjacent to the cathode. As shown in Fig. 4, the arc lines of potassium, rubidium, cesium, indium, and thallium give the opposite picture; their intensity reaches a maximum value near the lower electrode and in the central part of the flame. The intensity of thallium lines (Tl I 2767.87 and Tl I 3519.24) undergoes a second increase in the region lying near the cathode. The more difficult to excite lines of such elements as iron, nickel, titanium, etc., which can be superimposed on some of the analytical lines of the test elements are sharply weakened in the near-anode and central region of the flame, and are strengthened near the cathode.

As is evident from Fig. 5, the regions for the maximum isointensity of the rubidium lines and the cyanide bands are spatially separated in the arc flame; this makes it possible to choose the part of the flame with a low intensity for the cyanide bands and a sufficiently high intensity of the spectral lines of rubidium, and also of cesium, thallium, and indium. In order to find the isointensity regions in the arc flame, a technique of taking a section of the flame through the spectrograph slit was used [9].

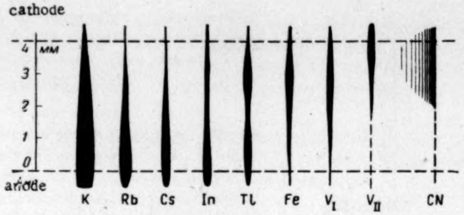

Fig. 4. Schematic distribution of the line intensities of various elements in the flame of a low temperature arc along the electrode axis: K I 4044.14 A; Rb I 4201.85 A; Cs I 4555.36 A; In I 4101.77 A; Tl I 3519.24 A; Fe I 4307.9 A; V I 3185.4 A; V II 3110.7 A; CN in the region 4200 A. The increase in line width here indicates an increase in intensity.

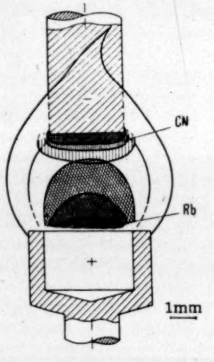

Fig. 5. Distribution of the intensity of the line Rb I 4201.85 and the CN band in the region 4200 A in the flame of a low temperature arc. The increase in the density of the shading signifies a doubling of intensity.

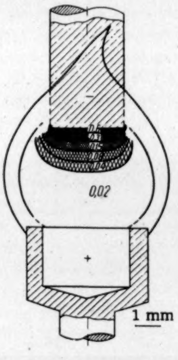

Fig. 6. Distribution of the relative intensity of the pair of lines V II 3110.7 and V I 3185.4 A in the flame of a low temperature arc.

Fig. 6 illustrates the distribution of the relative intensity of the spark and arc pairs of lines of vanadium II 3110.7 and V I 3185.4 in the arc cloud, as they react to the changes in the excitation conditions in the arc [10]. As is evident from this diagram, which illustrates the excitation conditions in the arc flame [10], on going from the lower electrode to the upper electrode there is observed an increase in the spark lines relative to the arc lines, which usually appear on increasing the temperature of the arc flame.

During the quantitative analysis of silicates for their content of Rb, Cs, Tl, and In, it is very essential that on introducing a large amount of potassium sulfate into the silicate, the temperature conditions of spectrum excitation which are established after starting the arc, are maintained throughout the whole period of effective passage of the group of elements to be determined into the discharge. Thus, the curve relating the temperature of the central part of the arc flame to the time of arc burning (Fig. 7) shows that, in the course of more than two minutes, there are no essential changes in the flame temperature during evaporation of mixtures of silicate powder with 50% K_2SO_4 on an electrode with the shape chosen. The beginning of the increase in flame temperature, and, consequently, the appearance in the spectrum of the cyanide bands, can, when necessary, be readily established from the sharp increase in potential across the electrodes [1].

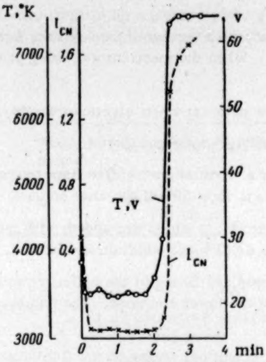

Fig. 7 Relation between the temperature and the intensity of the cyanide bands in the central part of the arc flame, and the duration of burning of the arc.

It is important to note that the intensity of the continuous background irradiated by the central part of the arc flame is, just like the intensities of the lines of Rb, Cs, Tl, and In, directly related to the concentration of potassium, and increases with increasing content of the latter in the melt. It is important also that the addition of sodium salts (Na_2SO_4, Na_2CO_3, and NaCl) to the samples, acts on the intensity of the cyanide bands in the same way as potassium sulfate. However, the effect of sodium salts, which have a higher ionization potential, is manifested less clearly. The values of the relative intensitites of the rubidium and cesium lines and of the background, which characterize the sensitivity of the spectrographic analysis, are 1.5 - 2 times less when sodium salts are added, than when potassium salts are added; suppression of the intensity of the cyanide bands is also less satisfactory when sodium salts are used instead of potassium salts.

The relation between the density of the background of the arc irradiated by the flame, and the potassium concentration of the silicate, makes it possible, when the test powder is diluted to the optimum amount with potassium sulfate, to use the background as an internal standard, and to determine rubidium and cesium in silicates with varying composition on the basis of the relative values of the intensities of their lines and of the background. The small dependance of the experimental results on changes in composition of the test silicate is illustrated by the calibration curves shown in Fig. 8. Under ordinary circumstances, for the determination in silicates of amounts of Rb and Cs which are not too small, the calibration curves are constructed within the coordinates: difference in blackening of lines and background — logarithm of the concentration of the element.

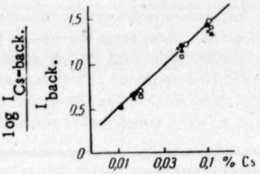

Fig. 8. Calibration curve for the determination of cesium in silicates on the basis of the Cs line I 4555.36 A.

● — SiO_2; × — SiO_2 (50%) + $Al(OH)_3$ (50%); ⊙ — SiO_2 (50%) + CaO (50%); ⊡ — SiO_2 (50%) + MgO (50%); ▲ — SiO_2 (50%) + Fe_2O_3 (50%)

Apparatus and Conditions for the Quantitative Spectrography in Rb, Cs, Tl and In in Silicate Ores and Minerals.

Spectrographic Apparatus. KS-55 autocollimating spectrograph with glass optics. The dispersion of the spectrograph in the 4000 A region was 5.9 A/mm. The part of the spectrum at 3500-4700 A was photographed. The slit width of the spectrograph was 0.020 mm.

Condenser Setup. A standard three-lens illuminating system with an intermediate image of the source in the plane of the diaphragm. Diaphragm height 5 mm, width 10 mm.

Photographic materials. Isoorthochromatic photographic plates with a sensitivity of 65 GOST units, contrast, size 9 · 24 cm; developer – standard metol-hydroquinone.

Spectrum excitation source. A vertical d.c. carbon arc supplied with a current of 5± 0.4 amp, from a mercury rectifier with an output potential of 160 volt; arc gap 4-5 mm. When the spectrum was being photographed (2 minutes), the arc was stabilized with K_2SO_4.

Arc electrodes. Carbon, spectrographically pure, upper electrode–cathode; lower electrode–anode (Fig.1).

Measuring apparatus. Non-recording MF-2 microphotometer and PS-18 spectroprojector.

Buffer material. Powdered potassium sulfate (chemically pure or analytical grade) free from traces of the elements to be determined was added to test materials and standards to form 50% of the total amount.

Standard samples. Powdered quartz or some other appropriate material to which was added, with successive dilution and grinding, 0.03-0.0003% thallium and indium, and 0.1-0.001% of rubidium and cesium.

Analytical samples. 40 mg of a mixture consisting of 20 mg sample and 20 mg of the buffer material (K_2SO_4), ground to pass 200 mesh; the aliquots were placed in the cup of the lower electrode. The number of parallel samples taken was three.

Exposure time for the spectra of samples and standards under the conditions indicated was 2 minutes.

Below are given the characteristics of the recommended analytical lines of the elements to be determined, and the conditions under which they are used; for convenience, the interfering lines of foreign elements and the control lines of the latter are also included. In practice, it is only superposition of the iron line on the rubidium line at 4201.85 that one has to deal with.

Rubidium. The main analytical line of Rb I 4201.85 (2.9 electron volt) can be located visually in the spectra of silicates containing about 0.0007 % Rb. Quantitative determination is carried out in the range 0.002-0.2% Rb. For amounts of iron up to 5-10% in the samples, this line is free from interference; above 10% the Fe line at I 4202.03 (4.44 electron volt) appears. The control line used was Fe I 4143.87, (4.45 electron volt) which was recommended by Ahrens [4]. At low rubidium contents, interference from iron can be removed by preliminary dilution of the sample with quartz; at higher concentrations, determination is carried out on the basis of another line of rubidium Rb I 4215.56 (2.9 electron volt), which is less intense but is free from interference by iron as long as the content of the latter does not exceed 30%. During the analysis of certain micas using this line, it is also necessary to take into account the possibility of the superposition of the strontium line Sr II 4215.56 on it; the latter appears at high strontium concentrations in the sample. Rubidium can be determined at high iron and strontium contents under the same conditions, on the basis of the line Rb (4201.85 by means of an ISP-51 three-prism glass spectrograph with an autocollimating UF-85 camera (dispersion 2.5 A/mm), which makes it possible to separate the interfering line of iron from the rubidium line.

Cesium. Determination is carried out on the basis of the line Cs I 4555.36 (2.7 electron volt), which appears in the sprectrum when about 0.001-0.003% of Cs is present. This element is determined quantitatively in the range 0.005-0.2% Cs. The arc line of titanium at Ti I 4555.49 (3.56 electron volt) may superimpose the cesium line for a titanium content of more than 5-10% in the sample; titanium is controlled by the appearance of the line Ti 4548.77 (3.55 electron volt). The less sensitive cesium line Cs I 4593.13 (2.7 electron volts) which appearas in the spectrum around 0.01% Cs can be used for the determination of 0.05-0.5% Cs. It is not superimposed by interfering lines.

Thallium. The line Tl I 3775.72 (3.3 electron volt) with a sensitivity of 0.0001-0.0003% Tl is used for the quantitative determination of 0.0003-0.02% of Tl in silicates, and also in non-silicate and monomineral samples when standards of the appropriate composition are used. In rare cases superposition of the thallium line by the nickel line Ni I 3775.57 (3.76 electron volt) is possible, when the sample contains more than 1-3% of nickel. The control line for nickel is Ni I 3807.1 (3.67 electron volt). The other thallium line Tl 3519.24 is less sensitive and has no advantages over the first line, since it also coincides with a nickel line.

Indium. There are two analytical lines for indium of almost equal value from an analytical point of view; these are In I 4511.32 (3.0 electron volt) and appear in the spectra of silicates at concentrations of 0.0001-0.0003% of In; they are used for the direct determination of indium in silicates and other materials, as long as its content does not exceed 0.02%. The indium line In 4101.77 is only unsuitable in the case of analysis of molybdenum-containing minerals, while the line In 4511.32 may be crossed by the lines of tin and titanium during the analysis of minerals of these elements.

Test element	Composition of the sample(standard)	Taken, %	Found, %	Relative error,%
Tl	Quartz	0,00050	0,00054	+8
	The same	0,00074	0,00075	+1
	" "	0,00074	0,00071	−4
	Quartz with 50% Fe_2O_3	0,0011	0,0011	0
	" " ZnS	0,0011	0,0011	0
	" " PbS	0,0011	0,0007	−36
	Silicate ore with FeS_2	0,0015*	0,0013	−13
	The same	0,007*	0,006	−14
	Quartz	0,0022	0,0022	0
	The same	0,0067	0,0069	+3
	" "	0,020	0,019	−5
In	Feldspar	0,00012	0,00014	+16
	The same	0,00037	0,00045	+21
	"	0,010	0,011	+10
	"	0,029	0,027	−7
	Silicate ore	0,0033*	0,0032	−3
Rb	Quartz	0,0054	0,0058	+7
	The same	0,011	0,011	0
	Quartz with 50% $Al(OH)_3$	0,016	0,018	+12
	The same	0,11	0,10	−9
	Quartz with 50% MgO	0,016	0,015	−6
	" " CaO	0,050	0,048	−4
Cs	Quartz	0,011	0,010	−9
	The same	0,016	0,017	+6
	Quartz with 50% $Al(OH)_3$	0,016	0,016	0
	" " MgO	0,016	0,014	−12
	" " Fe_2O_3	0,016	0,018	+12
	" " MgO	0,050	0,042	−16
	Quartz	0,11	0,10	−9
	Quartz with 50% CaO	0,11	0,11	0
	" " CaO	0,016	0,013	+18
	" " Fe_2O_3	0,11	0,10	−9

*Result of a chemical determination.

EXPERIMENTAL PROCEDURE

The prepared analytical sample (40 mg of mixture containing equal amount of test silicate and potassium sulfate) was placed in the crater of the lower electrode. The arc was fired with a short-time high frequency spark from an activator and 3-4 seconds afterwards exposure of the spectrum emitted by the central part of the flame was commenced; the exposure time was 2 minutes, in the course of which there occurred a sufficiently complete fractional evaporation of the elements to be determined. About 50 spectra were photographed on one plate (12 samples and 4-5 standards three times each); for the determination of only one of the elements, the number of spectra photographed on a plate can be increased, if the length of spectral part be cut down by means of a screen, and a 9 × 12 cm plate is shifted inside the casette.

The spectrograms were developed as usual until the blackening of the background was not less than 0.4.

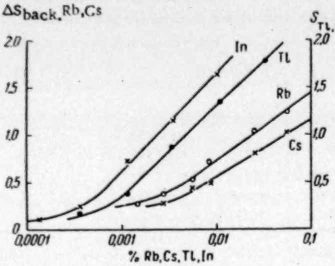

Fig. 9. Calibration curves for the determination of Rb, Cs, Tl, and In in silicates: Rb I 4215.85 A; Cs I 4555.36 A; Tl I 3775.72 A; In I 4101.77 A.

On the basis of the photometric measurements of the spectra of the standards, calibration curves were constructed for each plate within the coordinates: difference between blackening of the line and background—logarithm of the concentration (determination of rubidium and cesium) or in the coordinates: line blackening—logarithm of the concentration (determination of thallium and indium). For determination of higher concentrations of the elements than are indicated for the recommended analytical lines, the samples could be diluted accordingly with quartz or a dead rock.

Reproducibility and Accuracy of the Method

The reproducibility of the determination of rubidium, cesium, thallium, and indium was established by repeated analysis of standard powders of silicates, containing various amounts of these elements, and also by repeated analysis of natural minerals. Calculation of the probable experimental error for the elements in silicates (mean of three parallel determinations) showed that the reproducibility of the determination of these elements amounts t ± 8-9% for rubidium, cesium, and thallium and to ± 11% for indium. Typical working calibration curves for the determination of the listed elements, constructed on a silicate base, are shown in Fig. 9.

As noted already, on diluting the silicate powders with an equal weight of potassium sulfate, the results of the determination were not found to depend on the composition of the test silicate in the case of determination of rubidium and cesium, during the determination of indium and thallium, however, it was found that changes in the composition of the test materials, when one batch of standard samples was used, could lead to systematic deviations of up to 20-40%. This was found to be particularly true for the analysis of silicates containing up to 50% and more of galenite, calcium oxide, and certain other compounds. In such cases, and also where it is necessary to determine indium and thallium in non-silicate mono-mineral samples, it is recommended that samples of the appropriate bulk composition be used. For example, the table contains results for control analyses of silicates for their contents of rubidium, cesium, thallium, and indium.

SUMMARY

A low temperature d.c. carbon arc is a valuable excitation source of the spectra of Rb, Cs, Tl, and In under conditions which ensure the intensive passage of predominant amounts of potassium vapor into the arc discharge.

A method for the quantitative spectrographic determination of Rb, Cs, Tl, and In based on excitation of the spectra of these elements in a low temperature arc, permits the direct, simultaneous determination of low concentrations of Rb, Sc, Tl, and Cs in silicate powders, with a probable error of ± 9-11%.

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DETERMINATION OF CALCIUM, STRONTIUM, AND MAGNESIUM BY RADIOMETRIC TITRATION WITH COMPLEXON

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Various precipitation reactions [1-8] and reactions for the formation of extractable complex compounds [9, 9a] are used in the radiometric method of tritation.

The aim of the present work was to find a method for radiometric titration using complex forming reagents. This problem was solved by using non-isotopic indicators in the form of precipitates. The principle of the method is as follows. Let us assume that titration of the cation M^{2+} with reagent A^{2-} proceeds according to the following equation:

$$M^{2+} + A^{2-} \rightleftarrows [MA]. \tag{1}$$

The titration endpoint is established by means of a radioactive cation M_i^{2+}, found in the form of a precipitate M_i^*, which, on termination of reaction interacts with the complex forming reagent according to the equation:

$$M_i^* B + A^{2-} \rightleftarrows [M_i^* A] + B^{2-}. \tag{2}$$

The stability of the compound MA formed according to equation (1) is characterized by the value pK_{MA}. The equilibrium of reaction (2) is determined by the instability constant $K_{M_i^*A}$ of the complex $[M_i^*A]$ and the solubility product $L_{M_i^*B}$ of the precipitate M_i^*B.

Titration is possible when the logarithms of the instability constant of the complexes [MA] and $[M^*A]$ satisfy the following inequality:

$$pK_{MA} > pK_{M_i^*A}. \tag{3}$$

On the other hand, the relation between the instability constant of the complex $[M_i^*A]$ and the solubility product of the precipitate M_i^*B should be such that the precipitate can dissolve the complex forming reagent. When this titration is realized, reaction (1) begins. The radioactivity of the solution separated from the precipitate remains constant, and is determined by the amount of radioactive ions $M_i^{*\,2+}$ passing into solution in accordance with the solubility product of the precipitate M_i^*B. As soon as all the ions M^{2+} from the solution have reacted with the A^{2-} ions, excess of the latter will react with the M_i^{2+} ions of the precipitate; during this process the precipitate M_iB will gradually dissolve. Thus, the radioactivity of the solution will increase in proportion to the amount of the reagent introduced after the equivalence point has been reached. The theoretical titration curve is shown in Fig. 1.

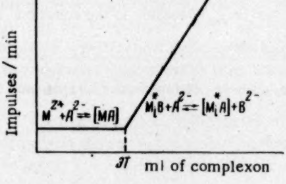

Fig. 1. Theoretical titration curve.

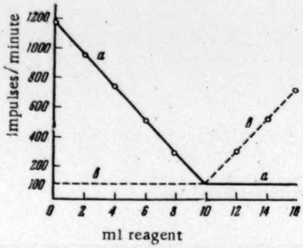

Fig. 2. a) Titration of 10 ml of 0.1 N Ag^*NO_3 with 0.1 N KIO_3 solution; b) titration of 10 ml of 0.1 N KIO_3 with Ag^*NO_3 solution.

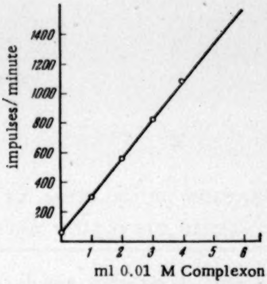

Fig. 3. Titration curve of Ag^*IO_3 with Complexon III at a pH of 10.5.

On the basis of this principle it should be possible to carry out radiometric titrations with any complexing agent which quantitatively reacts with the ions of the element to be determined. Below are given examples of the application of this principle to titration with Complexon III.

Ag^{110} in the form of silver iodate was used as the radioactive indicator in the precipitate.

A Study of the Behavior of the Indicator

pL for silver iodate is 7.3 [10]. The curve for the radiometric titration of Ag^*NO_3 with a solution of KIO_3, and a solution of KIO_3 with a solution of Ag^*NO_3 is shown in Fig. 2.

In order to shift the equilibrium $Ag^*NO_3 \rightleftharpoons IO_3^- + Ag^*$ to the left, excess iodate is added to the solution. Dissolution of silver iodate in the presence of Complexon III proceeds according to the equation:

$$Ag^*IO_3 + [H_2Y]^{-2} \rightleftharpoons [HAg^*Y]^{2-} + IO_3^- + H^+.$$

The position of the equilibrium of this equation is determined by the value of pL for Ag^*NO_3 and by the instability constant of the compound formed between silver and Complexon III.

The position of the equilibrium $[HAg^*Y]^{2-} + H+ \rightleftharpoons [H_2Y]^{2-} + Ag^{*+}$ depends on the pH of the solution. For silver complexonate pK = 7.3 [11].

Titration in a strongly alkaline medium is not recommended because of the conversion of silver iodate into silver oxide. The solubility of silver iodate in Complexon III depends on the pH. The optimum pH range for carrying out the titration of any ion, on observing the condition $pK > pK_{[HAg^*Y]^{2+}}$, is 9.5-11.5.

In this pH range, the reaction between silver iodate and Complexon III is quantitative. The radioactivity of the solution increases during the interaction of silver iodate and Complexon III (Fig. 3).

From Fig. 4 it is clear that the reaction between Ag^*IO_3 and 0.01 M Complexon III finishes after 0.5 minute when the solution is mixed; when 0.001 or 0.0001 M Complexon III solution is used, the time taken by the reaction increases.

We have studied the effect of those anions which can precipitate silver, e.g., according to the equation:

$$2[HAg^*Y]^{2-} + MoO_4^{2-} + 2H^+ \rightleftharpoons 2[H_2Y]^{2-} + Ag_2^*MoO_4.$$

Experiment showed that ions of molybdic, phosphoric, tartaric, and citric acids do not interfere. Cl^- ions interfere.

Titration can be carried out by direct, reverse, and indirect methods.

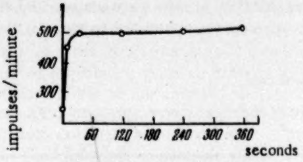

Fig. 4. Effect of duration of stirring on the rate at which silver iodate dissolves in the complexon.

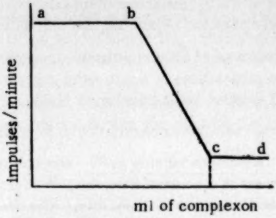

Fig. 5. Theoretical curve for back titration.

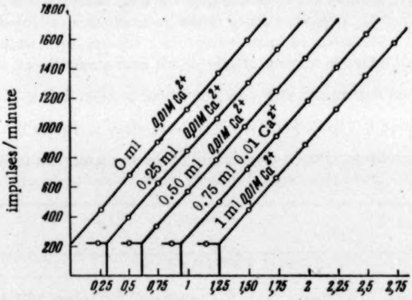

Fig. 6. Curves for radiometric titration of various amounts of Ca.

Direct titrations. Direct titration with complexon is possible of such ions which at pH 9.5-11.5 do not hydrolyze, or are kept in solution in the presence of masking agents (Mg, Sr, Ca, Co, Ni, Cu, Zn, Cd, In, Pb [12]). We have carried out direct titration of Mg, Sr, and Ca.

Reverse (back) titrations. Some elements, such as Th, Zr, Hg, and Bi cannot be kept in solution at a pH of 9.5-11.5. They can be determined by a back titration. For this purpose excess Complexon III is added to the test solution at a reduced pH and then the pH adjusted to 9.5-11.5, after which the indicator ($Ag^{*}NO_3$) is added. Part of the excess complexon dissolves the silver iodate, and the solution acquires a high activity. After this, excess complexon is titrated with a solution of the salt of any element which forms a less stable complexonate with the complexon than the test ion. During back titration, initially only the free complexon reacts. During this time the radioactivity of the solution remains constant (Fig. 5 a-b): subsequently, as the solution is added the silver complexonate decomposes and the Ag^{*} passes into the precipitate, while the radioactivity of the solution decreases proportionally (Fig. 5 b-c); when all the silver complexonate has decomposed, the radioactivity of the solution remains constant (section c-d).

Indirect titration. Quantitative determination of anions is possible by means of indirect titration. For this purpose the test ion is precipitated with a suitable cation, which is subsequently titrated with complexon. The precipitate obtained is dissolved and the given cation titrated.

Reagents and apparatus. 0.01 M Complexon III was prepared by dissolving an accurately weighed amount of the pure compound. The compound was dried beforehand for several hours at 80°. The solution was neutralized by means of NaOH (the tetrasodium salt is obtained). More dilute solutions of Complexon III (0.001 and 0.0001 M) were prepared by diluting the 0.01 M solution.

0.1 M solutions of calcium, nitrate, magnesium sulfate, and strontium nitrate were prepared by dissolving the crystalline preparations in water. The concentration of these solutions was established by titration with the Complexon III solution using eriochrome black T as indicator.

A saturated solution of chemically pure potassium iodate was used.

Silver nitrate with labeled Ag^{110} was obtained by irradiating chemically pure $AgNO_3$ in a IFA atomic reactor for 5 hours in a neutron beam of 10^{10} neutrons/second/cm^2. The irradiated $AgNO_3$ was dissolved in sufficient water to give a 0.01 N solution. The precipitate of silver iodate obtained on precipitating 5 ml of Ag^*NO_3 by means of 3 ml of potassium iodate had low radioactivity (Fig. 2). On addition of 1 ml of 0.01 M Complexon III solution the radioactivity of the solution increased by 250 impulses/minute.

The usual apparatus was used for the radiometric measurents. β- and γ radiations were measured by means of an MS-7 counter in a B-2 setup. Titration was carried out by means of 1 and 2 ml automatic microburets. The solutions were mixed by means of a magnetic stirrer. The pH was measured with universal indicator paper.

Titration of Ca, Sr, and Mg in pure solutions. 5 ml of the 0.01 N solution of active silver nitrate and 3 ml of saturated potassium iodate solution were pipetted into a 200 ml beaker. After 1 minute, various amounts of the solutions of the Ca, Sr, and Mg salts were added to the beaker from a microburet. The volume of the solution was made up to 50 ml with deionized water, stirred for 2 minutes, after which its radioactivity was measured. The complexon was added in aliquots of 0.1-0.3 ml from a microburet.

The equivalence point was determined either graphically or by calculation.

The titration curve is shown in Fig. 6, while the results are given in Tables 1-3.

The sensitivity of the method depends on the activity of the indicator. On increasing the activity, the sensitivity also increases.

TABLE 1

Ca, mg			
taken	found	taken	found
5,83	5,79	0,44	0,45
1,75	1,70	0,44	0,43
1,75	1,72	0,29	0,30
1,17	1,15	0,29	0,29
1,17	1,15	0,29	0,29
1,17	1,13	0,15	0,15
0,58	0,56	0,15	0,14
0,58	0,59	0,15	0,14

Titration of magnesium in the presence of calcium. During complexonometric determination of Ca and Mg it is necessary to separate them [11-15]. During separation of these elements by the sulfite method, poor results are obtained since the indicator works poorly in a sulfite medium. Separation of Ca and Mg by precipitating the calcium with molybdate gave good results. The presence of MoO_4^{2-} ions in the solution being titrated does not interfere with the determination. For determination of calcium and magnesium (in dolomites, limestone, glass, pharmaceutical preparations, etc, and also for determination of water hardness) the following procedure can be adopted. Total Ca + Mg is determined in one aliquot of the solution, while magnesium is titrated in another aliquot after precipitation of calcium as molybdate. Calcium is determined by difference.

EXPERIMENTAL PROCEDURE

Solutions containing Ca + Mg in various amounts are adjusted to a pH of 8-9 by addition of KOH. The solution is then heated to 60-70° and 10 ml of a 10% solution of potassium molybdate added with continuous stirring over a period of 1-2 minutes, after which the solution is brought up to the boiling point for 2-3 minutes. The precipitate is filtered off through filter paper (Schleicher-Shcul No. 598, blue band) and the precipitate washed with 10 ml of distilled water and then with 5% ethanol solution. The indicator (Ag^*NO_3) is added and the volume of the solution made up to 50 ml with water; the magnesium is then titrated with Complexon III as indicated above. The results obtained are given in Table 4.

TABLE 2

Sr, mg	
taken	found
9,04	8,84
6,78	6,78
4,52	4,42
3,62	3,62
2,71	2,61
2,26	2,26
1,81	1,81

TABLE 3

Mg, mg	
taken	found
1,60	1,52
0,51	0,52
0,32	0,32
0,32	0,32
0,16	0,15
0,16	0,17
0,11	0,11

TABLE 4

Ratio of Ca:Mg	Mg, mg	
	taken	found
1 : 1	0,32	0,32
2,5 : 1	0,32	0,32
5 : 1	0,32	0,28
10 : 1	0,32	0,31
20 : 1	0,32	0,32
30 : 1	0,32	0,28

SUMMARY

A method has been developed for radiometric titration by means of complexing agents, precipitates being used as non-isotopic indicators.

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COLOR REACTIONS FOR SCANDIUM

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Very few color reactions are known for scandium. Such reactions are not mentioned in the literature [1-3]; one or two color reactions for scandium are briefly mentioned in some papers [4-6]. In acid media, scandium, and also thorium, zirconium, cerium, etc., give a rose-colored precipitate with 2,5-dihydroxy-1,4-benzoquinone [7], and a dark-violet precipitate with sodium alizarin sulfonate [8-11]. Quinalizarin [8, 12] and cochineal [8], among other hydroxyanthraquinones, have been suggested as color reagents for scandium.

We decided it would be advantageous to study the behavior of a number of hydroxyanthraquinones, and also of naphthazarine towards scandium under various conditions, and to compare them with reagents suggested earlier.

The reactions were carried out as follows. To 0.2 ml of a solution of a scandium salt was added 0.1 ml of a buffer solution with a known pH value, and 0.1 ml of a 0.1% aqueous or alcoholic solution of reagent; a blank test was carried out in parallel (Table 1).

TABLE 1

Reactions of Scandium Salts with Hydroxyanthraquinones

Reagent	pH	Color of the solution		Limiting concentration
		Control	Scandium	
Alizarin S	1—5	Yellow	Red	1 : 300 000
Quinizarin	4	Yellow	Orange	1 : 200 000
	5—8	The same	Violet	1 : 300 000
	9—11	» »	The same	1 : 300 000
Purpurin	1	Yellow	Red	1 : 40 000
	2—5	The same	The same	1 : 500 000
	6—7	Rose	» »	1 : 500 000
	8	The same	» »	1 : 80 000
Anthracene blue WR	3—5	Orange	Violet	1 : 300 000
	6	Red violet	The same	1 : 200 000
	7—9	The same	» »	1 : 80 000

Of the hydroxyanthraquinones tested, the most sensitive reagents are purpurin and alizarin S, which give positive results at a pH of 5 and lower, and also anthracene blue WR at pH 3-5. Only a few other cations (Th^{IV}, Zr^{IV}) are capable of giving a color reaction at low pH values. Alizarin and chrysazine give a color reaction with scandium, but this reaction is given at high pH values, at which many other cations such as yttrium, lanthanum,

TABLE 2

Reactions of Scandium Salts with Azo Dyes

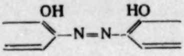
Azo dye	pH	Color of the solution		Limiting concentration	Cations which give the same or a similar reaction
		control	scandium		
Metachrome olive-brown	2 — 4	Yellow	Rose	1 : 150 000	Th, La,
	5 — 8	"	"	1 : 300 000	Th, La, Y
Acid monochrome olive J	1 — 2	Yellow	Rose	1 : 80 000	Th
	3 — 4	" "	"	1 : 300 000	Th, Ce, Y, Al
	5 — 9	" "	"	1 : 150 000	Th, La, Ce, Y, Al
Acid chrome dark green S	2	Violet	Blue	1 : 10 000	Th
	3 — 5	"	"	1 : 200 000	Th
	6 — 7	"	"	1 : 300 000	Th, Y
Acid monochrome Z	7 — 8	Violet	Rose	1 :1000 000	Th, La, Ce, V, Al
Acid chrome black S	4	Yellow	Red	1 : 10 000	Th, La, Y
	5	"	"	1 : 80 000	Th, La, Y
	6	"		1 : 150 000	La, Ce, Y
	7 — 9	"	"	1 :1000 000	La, Ce, Y
Acid chrome blue-black K	1	Red	Red-violet	1 : 10 000	—
	2 — 5	"	"	1 : 150 000	—
	6 — 7	"	"	1 : 200 000	La, Y, Al
Acid monochrome green S	3	Violet	Blue	1 : 80 000	Th
	4 — 5	"	"	1 : 150 000	Th
	6 — 9	"	"	1 : 200 000	—

cerium, aluminum, etc. interact. Naphthazarin, quinalizarin, chrysazin, and gallein proved to be comparatively insensitive reagents for scandium. Far from all the sensitive reagents permit the determination of scandium in the presence of other cations. By making use of the fact that quinizarin gives a violet color with scandium salts at a pH of 6-9, while thorium, yttrium, lanthanum, and cerium salts give an orange color, it is possible to detect scandium in the presence of the cations indicated in amounts which are 30-70 times that of the scandium. The other hydroxyanthraquinones do not permit detection of scandium in the presence of thorium. Scandium can be detected in the presence of 10-50 times its amount of yttrium, lanthanum, cerium, and aluminum by means of purpurin (pH 2-3), and alizarin (pH 1-3). Trivalent iron interferes with detection of scandium by means of hydroxyanthraquinones.

The reaction for scandium, thorium, yttrium, etc. proved applicable to the development of paper chromatograms.

Azo dyes are still little used as reagents for scandium. Kuznetsov [13] has indicated that 2-hydroxynaphthalene-(1-azo-2)-naphthalene-1'sulfonic acid is capable of giving a color reaction in a weakly alkaline medium with the salts of many metals, including scandium. Benzene-2-carboxylic acid-(1-azo-2') chromotropic acid, in neutral media, gives a color reaction with salts of scandium, thorium, the rare earths, etc.[14]. 1-(2-Pyridylazo)-2-naphthol gives a color reaction with the salts of scandium, lanthanum, zinc, nickel, lead, etc. [15].

We have studied the behavior of a number of azo dyes towards scandium salts, bearing in mind in the first instance, 1,1-dihydroxy azo dyes containing the atomic group



Such compounds, according to Kuznetsov [16], are capable of giving color reactions with aluminum salts. It might be assumed that scandium, which is also an element belonging to Group III of the periodic system will also react with these reagents, but possibly at other pH values. The reactions were carried out in a micro test tube by mixing 0.05 ml each of a solution of a scandium salt, a buffer solution, and a 0.1% solution of the azo dye. We studied 28 dyes containing this group of atoms, and found that they all gave color reactions with scandium salts; this confirms the hypothesis advanced above. In Table 2 results are given for only some of the compounds which are capable of giving a reaction which is sufficiently sensitive at low pH values.

Most of the azo dyes tested start to react with scandium salts at pH 2-3; the maximum sensitivity is mainly observed at pH 6-7. The nature of the precipitates observed at pH's higher than 8 is not given in Table 2 since many cations give this reaction under these conditions.

Certain azo dyes, at low pH values, permit scandium to be distinguished from thorium and the rare earths. Using acid chrome blue black K it is possible to detect scandium (pH 2-3) in the presence of 7 times its amount of lanthanum or yttrium, and 100 and 300 times its amount of cerium and aluminum respectively. The reaction with acid monochrome green S permits detection of scandium in the presence of 30 times its amount of thorium, and 1500 times its amount of lanthanum and other elements (pH 6).

SUMMARY

Color reactions for scandium with hydroxyanthraquinones and 1,1'-dihydroxyazo dyes have been studied. New reagents are suggested for scandium, some of which are characterized by high sensitivity and permit detection of scandium in the presence of the salts of other elements.

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RESEARCH INTO THE ANALYTICAL CHEMISTRY OF THALLIUM

COMMUNICATION 3. SPECTROPHOTOMETRIC DETERMINATION OF THALLIUM WITH ANTIPYRINE DERIVATIVES*

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The iodide complexes of thallium, in contrast to the chloride and bromide complexes, have a yellow color. In a solution containing Tl^{III} and excess of iodide ions, a number of equilibria exist [1]:

$$Tl^{3+} + 21 \rightleftharpoons Tl^{+} + I_2$$

$$I_2 + I^{-} \rightleftharpoons I_3^{-}$$

$$Tl^{+} + I_2^{-} + I^{-} \rightleftharpoons$$

On gradual addition of a KI solution to a dilute (10^{-4} - 10^{-5} M) solution of $Tl_2(SO_4)_3$, these reactions proceed in the sequence indicated above, while the equilibrium of the first reaction, as a result of the large difference in the normal oxidation–reduction potentials of the system $Tl^{3+}/Tl^{+} = 1.22$ volt, and $I_2/2I^{-} = -0.54$ volt [2] is shifted almost completely to the right. The absorption maximum of solutions containing the triodide ion ($\lambda = 360$ mμ) in the presence of Tl^{3+} and excess KI is shifted into the longer wavelength side of the spectrum ($\lambda = 395$ mμ). But the TlI_4^{-} ion is strongly dissociated in aqueous solution, and the optical density of solutions containing Tl^{3+} and I^{-} only becomes constant at a molar ratio of thallium to iodide of 1:3000 (thallium concentration 2-10 γ/ml). Accordingly, spectrophotometric determination of thallium in the form of TlI_4^{-} has proved to be possible only at high KI concentrations in the solution–about 5% [1]. This is a big drawback in practical work, since I^{-} is rapidly oxidized to I_2 in concentrated solution, while addition of $Na_2S_2O_3$ leads to complete disappearance of the color of the solution, the latter being related to the shift of the equilibrium toward formation of univalent thallium. Extraction of iodine with chloroform and benzene has the same effect.

In order to increase the stability of TlI_4^{-} ions at low KI concentrations, its precipitation with antipyrine derivatives – diantipyrylmethane and diantipyrylpropylmethane – was undertaken.

It was established that in acid media, in the presence of KI, thallium III is precipitated quantitatively by the bases mentioned. The compounds formed are extracted by benzene, chloroform, and dichloroethane to give a yellow colored extract, which served us as a basis for developing a spectrophotometric method of determining thallium.

In order to establish the nature and composition of the compounds formed, the compound obtained by precipitation of the iodide complexes of thallium with diantipyrylmethane was isolated in the pure sate by the following method: to a solution containing about 0.02 g of thallium in the form of $Tl_2(SO_4)_3$ was added 20 ml of HCl (1:1), this was followed slowly, with stirring, by 20 ml of 0.5% KI, and 5 ml of a 1% solution of diantipyrylmethane; the yellow precipitate formed was filtered off and washed with water. After recrystallization from acetone, dark-red needles were obtained. The thallium and iodine content of the isolated compound was determined: thallium was determined by precipitation and weighing as TlI, after dissolving an accurately weighed aliquot in acetone and adding a small excess of KI and a 5% solution of $Na_2S_2O_3$ until the solution was decolorized; iodine was determined by precipitation and weighing as AgI. The analytical results confirmed that thallium is precipitated as $C_{23}H_{24}O_2N_4 \cdot HTlI_4$.

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*For Communication 2 see J. Anal. Chem. 14, 28 (1959).

**Student L. M. Afanas'eva participated in the work.

Calculated for $C_{23}H_{24}O_2N_4 \cdot HTlI_4$: Tl 18.56%; I 46.10%; Found % Tl 18.58%; 19.12; I 46.71, 46.14.

Isolation of the product formed by precipitating the iodide complexes of thallium with diantipyrylpropylmethane in a pure state proved impossible; the iodide of the base itself separates out at the same time.

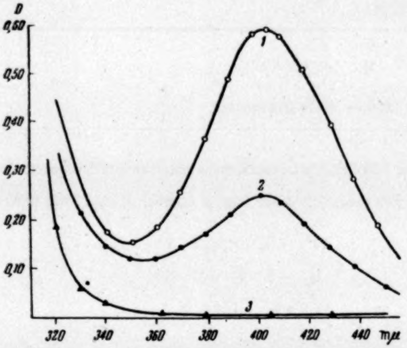

Fig. 1. Absorption curves for the iodide complexes of trivalent thallium with antipyrine derivatives: Curve 1. 4.8 · 10^{-5}M $C_{23}H_{24}O_2N_4 \cdot HTlI_4$ in benzene; Curve 2. Absorption of a benzene solution obtained on extracting Tl^{3+} from a solution containing KI and diantipyrylpropylmethane (thallium concentration 1.96 · 10^{-5} M). Curve 3. Absorption of a benzene solution obtained on shaking benzene with an aqueous solution of KI and diantipyrylpropylmethane.

In order to determine the spectrophotometric characteristics of the compounds obtained, 13.2 mg of $C_{23}H_{24}O_2N_4 \cdot HTlI_4$ purified by recrystallization and dried in air was dissolved in 250 ml of benzene and the absorption spectrum of the solution (Fig. 1, 1), taken on a SF-4 spectrophotometer with a cuvette having $l = 10$ mm. The molar absorption coefficient was found to be about 12.000 at 405 mμ. A similar absorption curve was also observed for a benzene solution obtained on extracting thallium from a solution containing KI and diantipyrylpropylmethane (Fig. 1, 2); the molar absorption coefficient was the same. Accordingly, the molecular weight of the base-precipitant of the iodide complexes of thallium (388.0 for diantipyrylmethane and 430.0 for diantipyrylpropylmethane) has no appreciable effect on the maximum and the value of the light absorption of the benzene solutions of the compounds obtained. The composition of the compound formed on precipitating the iodide complexes of trivalent thallium with diantipyrylpropylmethane was determined by the Ostromyslenskii—Job method, and by the method of continuously changing the concentration of one of the components. For work by the Ostromyslenskii—Job method, two series of isomolar solution were prepared; in one of these series, the molar ratio Tl:I was altered while the excess of precipitant used was kept constant as well as the acidity; in the other series, the molar ratio of thallium to diantipyrylpropylmethane was changed while the excess KI and the acidity were kept constant. The diantipyrylpropylmethane solution was prepared from an accurately weighed amount of reagent recrystallized from alcohol (m.p. of reagent 155-156°) and dried to constant weight at 130°. The $Tl_2(SO_4)_3$ solution was standardized complexonometrically [3].

First Series

I Series

0,0003631 *M* $Tl_2(SO_4)_3$, ml 10 9 8 7 6 5 4 3 2 1 0
0,0003631 *M* KI, ml 0 1 2 3 4 5 6 7 8 9 10

To each member of this series of solutions was added 1.2 ml of 1 N H_2SO_4 and 1 ml of 0.2% diantipyrylpropylmethane solution.

Second Series

II Series

0,0003631 *M* $Tl_2(SO_4)_3$, ml 10 9 8 7 6 5 4 3 2 1 0
0,0003631 *M* DAPM, ml 0 1 2 3 4 5 6 7 8 9 10

To each member of this series of solutions was added 1.2 ml of 1 N H_2SO_4 and 1 ml of 0.2% KI solution.

Each of the solutions from both series was extracted with 10 ml of benzene, and the optical density of the extracts measured in a cuvette with l = 10 mm in a SF-4 spectrophotometer at 400 and 410 mμ.

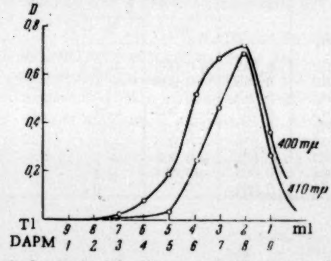

Fig.2. Optical density—composition curve for a constant concentration of diantipyrylpropylmethane.

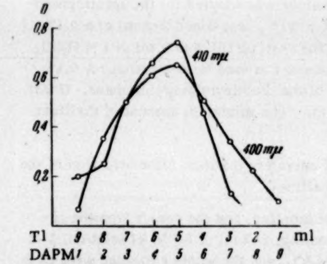

Fig. 3. Optical density—composition curve for a constant concentration of KI.

The experimental results (Figs. 2 and 3) show that the optical density maximum is observed at a ratio of Tl:I of 1:4 and at a ratio of Tl:diantipyrylpropylmethane of 1:2. Similar results were obtained when the method of continuous changes was used (Fig.4 and 5). To 6 solutions each containing 1 ml of 0.0003631 M $Tl_2(SO_4)_3$ were added 1,2,3,4,5, and 6 ml of 0.0003631 M of KI, followed by 1 ml of 1 N H_2SO_4, and 1 ml of 0.2% reagent solution, and the volume made up to 10 ml with water; the solutions were then extracted with 10 ml of benzene. The optical density became almost constant on reaching a ratio of Tl:I = 1:4.

In exactly the same way, solutions were prepared, each containing 1 ml of 0.0003631 M $Tl_2(SO_4)_3$, increasing amounts of diantipyrylpropylmethane (0.5, 1,2,3,4, and 5 ml of 0.0003631 M solution), and excess KI (1 ml of 0.2% solution). The total acidity was 0.1 N with respect to H_2SO_4. The optical density became almost constant for a ratio of Tl:diantipyrylpropylmethane = 1:1 (Fig. 5).

Comparison of all the results lead to the conclusion that the composition of the product formed corresponds to the formula $C_{26}H_{30}O_2N_4 \cdot HTlI_4$.

The results obtained testify to the high stability of $C_{23}H_{24}O_2N_4 \cdot HTlI_4$ and $C_{26}H_{30}O_2N_4 \cdot HTlI_4$; this means that these compounds can be formed, and make it possible to get a constant optical density for a comparatively small excess of KI and diantipyrylpropylmethane, compared with the amounts theoretically necessary.

It should be noted that the optical properties of the compounds described above (the position of the light absorption maximum and the value of the molar extinction coefficient) almost coincide with the optical

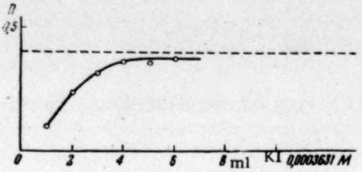

Fig. 4. Relation between optical density and KI concentration, when the thallium and diantipyrylpropylmethane concentrations are kept constant.

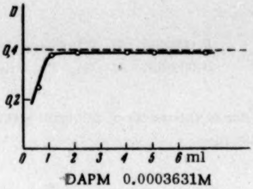

Fig. 5. Relation between optical density and diantipyrylpropylmethane concentration, when the Tl and KI concentrations are kept constant.

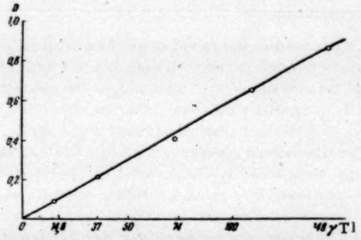

Fig. 6. Calibration curve for the spectrophotometric determination of thallium in the form in of $C_{23}H_{24}O_2N_4 \cdot HTlI_4$ or $C_{25}H_{30}O_2N_4 \cdot HTlI_4$ at 400 mμ, l = 10 mm.

TABLE 1

Determination of Thallium (I)

Tl taken, mg	Tl found mg	Error	
		mg	%
0,042	0,045	+0,003	+ 7
0,042	0,045	+0,003	+ 7
0,042	0,042	0	0
0,042	0,037	−0,005	−12
0,042	0,037	−0,005	−12
0,063	0,055	−0,008	−13
0,063	0,065	+0,002	+ 3
0,084	0,085	+0,001	+ 1
0,084	0,084	0	0

properties of the iodide complexes of trivalent thallium (I). A similar phenomenon is observed in the case of the optical properties of the complex ions of Co^{II} with SCN^- in the absence and in the presence of diantipyrylmethane [4]. However, the use of such bases as diantipyrylmethane and diantipyrylpropylmethane significantly increases the stability of the iodide complexes of thallium, and simplifies and considerably improves the technique for its determination.

On the basis of these preliminary experiments the following technique was adopted for the spectrophotometric determination of thallium (III); to a solution containing 10-200 γ Tl^{3+}, was added 2-3 ml of a 0.1% KI solution, 1-2 ml of a 0.05% solution of diantipyrylpropylmethane in CH_3COOH (1:10) and 1 ml of 1 N H_2SO_4. The total volume of the aqueous phase was about 10 ml. 10 ml of benzene was used for extraction. A 0.1% solution of diantipyrylmethane can be used with equal success instead of the diantipyrylpropylmethane. Under these conditions the color of the extracts conforms to Beer's law (Fig. 6). The minimum amount of thallium that can be determined is 0.3 γ Th/ml.

The method developed has been applied to the determination of univalent thallium after oxidation of the latter with bromine in a neutral or weakly acid medium to trivalent thallium.

To a solution containing univalent thallium was added 2-3 ml of bromine, and the excess bromine removed by boiling; to the solution containing $TlBr_3$ was added, after cooling, 2-3 ml of 0.1% KI solution, 1-2 ml of a 0.05% solution of diantipyrylpropylmethane, and 1 ml of 1 N H_2SO_4, and the whole extracted with 10 ml of benzene; the optical density was finally measured at 400 mμ. As the results given in Table 1 show, the method can be used for determining univalent thallium.

It was of considerable interest to establish the selectivity of this method of determining thallium, and particularly the possibility of determining this element in the presence of Cd, Bi, Cu, Zn, Fe, and also of Ga and In. Cu^{2+} and Fe^{3+} react with KI to liberate iodine, and this could lead to inaccurate results unless precautions are taken to prevent this reaction. Bismuth forms an intensely colored complex BiI_4^-, while cadmium forms a fairly stable complex CdI_4^-, which can also be precipitated by diantipyrylmethane and diantipyrylpropylmethane.

Tartaric acid and Complexon III were used for eliminating interference from Cu^{2+}, Fe^{3+}, and Bi^{3+}. Tartaric acid in a weakly acid medium (pH 2-3) eliminates the influence of Cu^{2+} and Bi^{3+}, but does not prevent interference from Fe^{3+}, which, under these conditions, passes into the extract and thereby enhances the intensity of the color of the benzene layer.

The most successful masking agent proved to be Complexon III, which forms at pH 2-3 with Cu^{2+}, Fe^{3+}, and Bi^{3+} stable compounds which do not interact with KI. Under these conditions, thallium (III) is more firmly bound in its compounds $C_{23}H_{24}O_2N_4 \cdot HTlI4$ and $C_{26}H_{30}O_2N_4 \cdot HTlI_4$, than in its compound with Complexon III.

To a solution containing Tl^{3+} and Me^{n+} (Cu^{2+}, Fe^{3+}, Bi^{3+}) was added a few milliliters of a 5% solution of Complexon III, ammonia was the added until the solution had a weak odor of the latter (the solution should remain clear during this stage; should a precipitate appear or a faint turbidity develop, additional Complexon III solution should be added); KI solution and the reagent were then added in the requisite amounts, after which the solution was carefully acidified to a pH of about 3, using universal indicator paper (it is best to use 2 M CH_3COOH). The final solution was extracted with benzene, and the optical density of the extract measured as usual on a SF-4 spectrophotometer at 400 mμ using a cuvette with a layer thickness of 10 mm.

Zn, In, and Ga ions, even in the absence of Complexon III, do not interfere with the spectrophotometric determination of thallium (Table 2). Cadmium does not interfere as long as its concentration is not too high (the ratio Tl:Cd should not exceed 1:200). When larger amounts of cadmium are present, the amount of KI and reagent used increases, and low results are obtained for thallium. In the presence of Complexon III, lead, even when it is present in amounts which are 20,000 times that of the thallium, shows hardly any effect at all (Table 2).

TABLE 2

Determination of Thallium in the Presence of Foreign Ions

Tl taken, mg	Me^{n+} taken, mg	Ratio Tl:Me	Tl found, mg	Error, mg
0,037	20 Cu	1:540	0,037	0
0,037	40 »	1:1080	0,037	0
0,037	20 Fe	1:540	0,037	0
0,015	80 »	1:5300	0,017	+0,002
0,022	100 »	1:4500	0,021	−0,001
0,022	20 Bi	1:1000	0,024	+0,002
0,037	40 »	1:1080	0,032	−0,005
0,037	20 »	1:540	0,036	−0,001
0,037	206 Zn	1:5570	0,037	0
0,037	206 »	1:5570	0,039	+0,002
0,037	2 In	1:54	0,036	−0,001
0,037	2 »	1:54	0,034	−0,003
0,037	2 Ga	1:54	0,035	−0,002
0,037	4 Cd	1:108	0,037	0
0,037	8 »	1:216	0,036	−0,001
0,037	10 »	1:270	0,032	−0,005
0,037	10 »	1:270	0,030	−0,007
0,037	200 Pb	1:5400	0,035	−0,002
0,015	200 »	1:13000	0,015	0
0,015	300 »	1;20000	0,013	−0,002

Hg^{2+} ions in the presence of excess KI give a soluble complex, which is precipitated by antipyrine derivatives; the precipitate is extracted by benzene to give a yellow colored extract; interference from mercury cannot be suppressed by addition of Complexon III under the conditions described above.

SUMMARY

It has been shown that antipyrine derivatives-diantipyrylmethane and diantipyrylpropylmethane—precipitate thallium (III) in the form of $C_{23}H_{24}O_2N_4 \cdot HTlI_4$ and $C_{26}H_{30}O_2N_4 \cdot HTlI_4$ in the presence of KI in an acid medium.

It has been established that the compounds $C_{23}H_{24}O_2N_4 \cdot HTlI_4$ and $C_{26}H_{30}O_2N_4 \cdot HTlI_4$ are extracted by benzene, and that the color of the extract conforms to Beer's law at 400-405 mμ.

The molar extinction coefficient of solutions of the compounds obtained in benzene is 12,000 at 400-405 mμ, and is independent of the molecular weight of the base-precipitant.

A method has been developed for the spectrophotometric determination of thallium in the presence of Fe, Bi, Cu, Zn, Pb, Cd, Ga, and In.

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*Original Russian pagination. See C. B. translation.

**In Russian.

QUANTITATIVE DETERMINATION OF THALLIUM AS DICHROMATE

COMMUNICATION 2. DETERMINATION OF THALLIUM IN THE PRESENCE OF OTHER ELEMENTS *

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The quantitative determination of thallium in the form of its dichromate has been discussed previously [1-2] as well as the possible application of this method. One of the main advantages of determining thallium as the dichromate is the possibility of determining it directly without preliminary separation from accompanying elements.

The present article is devoted to determination of thallium in the form of the dichromate in the presence of those metals which form, and those which do not form, sparingly soluble chromates.

Thallium dichromate was precipitated previously from sulfuric acid solutions [2]. Since some accompanying metals are precipitated by the sulfate ion, a study was made of the possibility of determining thallium in the form of dichromate in solutions of other mineral acids, in particular,in nitric and perchloric acids. This problem was also of independent interest. It is known [2] that non-reproducible results have been obtained during the determination of thallium by precipitating it from perchloric acid solutions [3]. Accordingly, we had to explain whether or not the acid and its concentration affect the precipitation of thallium dichromate.

Thallium was determined quantitatively by the gravimetric method [2].* The thallium dichromate was precipitated without heating from acid solutions by means of chromic oxide. In those cases where precipitation was carried out from sulfuric or perchloric acid solution, thallium sulfate was used as the original salt; during precipitation from nitric acid solution, the thallium salt used was the nitrate. The metals in whose presence thallium was determined were added beforehand, either in the forms of sulfates or nitrates respectively. Thallium dichromate was precipitated from a solution with a volume of about 80 ml; water was then added to bring the volume up to about 100 ml. The thallium dichromate precipitate was kept in the mother liquor for 3-4 hours at 1-3°, afterwards the precipitate was filtered through a No.4 glass crucible and washed. Initially the precipitate was washed free from the metals present during the determination of thallium by means of a cooled acid solution of chromic oxide, the concentration of which corresponded to that of the mother liquor (see Table 1) and then with a cooled solution of chromic oxide containing 1 g CrO_3 in 100 ml; it was finally washed with acetone until no chromate was detected in the wash liquor. The washed precipitate was dried to constant weight at 110-130° and weighed as $Tl_2Cr_2O_7$.

The results which are given in Table 1 indicate that it should be possible to determine thallium quantitatively as its dichromate in nitric and perchloric acids; the maximum permissible concentration of perchloric acids; the maximum permissible concentration of perchloric acid, as was the case when sulfuric acid was used [2], amounts to approximately 18-20 g per 100 ml of solution, while the amount of nitric acid is about 10 g per 100 ml. Thallium dichromate is also precipitated quantitatively at lower acid concentrations.

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*For Communication 1 see J. Anal. Chem. 13, 545 (1958).

**N. I. Solotina participated in the experimental work.

TABLE 1

Determination of Thallium as Its Dichromate in Nitric and Perchloric Acid Solutions

Taken, g/100 ml				Tl found, g*	Error, mg
Tl	CrO_3	HNO_3	$HClO_4$		
0,0767	1	5	—	0,0766	—0,1
0,0767	1	10	—	0,0766	—0,1
0,0767	3	15	—	0,0757	—1,0
0,0767	8	15	—	0,0758	—0,9
0,0810	1	—	1	0,0810	0,0
0,0810	1	—	5	0,0808	—0,2
0,0810	1	—	10	0,0809	—0,1
0,0810	2,5	—	18	0,0810	0,0
0,0810	3	—	20	0,0810	0,0
0,0810	8	—	25	0,0802	—0,8

*Mean value of several determinations.

Determination of Thallium in the Presence of Metals which do not Form Sparingly Soluble Compounds

Thallium was determined quantitatively in the form of its dichromate in the presence of Zn, Cd, Fe, Cu* , Al, Mg, Co, Ni, Sb, In* , Ga, Ge, and Tl^{III} (Tables 2-3). The results obtained show that it is possible to determine thallium directly as its dichromate in acid solutions when the metals indicated are present, individually, or together. It follows naturally that other metals, which, under the experimental conditions used for determining thallium, do not form sparingly soluble compounds, and are not coprecipitated with $Tl_2Cr_2O_7$, will not interfere with thallium determination either.

It should be observed that results for determination of thallium in the presence of Fe^{III} at relatively high acid concentrations are on the low side when the thallium dichromate precipitate is kept for a long time in contact with the mother liquor, e.g., overnight, which is quite permissible in other cases. This is connected with the oxidation—reduction reaction between Tl^{I} and Fe^{III} [4,5]. Accordingly, when thallium is determined in the presence of Fe^{III}, precipitation must be carried out in the cold and the precipitate filtered off after 3-4 hours (depending on the technique).

In those cases where thallium is determined in the presence of divalent iron, excess chromic oxide is necessary (to oxidize the iron) and the precautions taken in the presence of ferric iron observed, since the latter is formed during the oxidation. The fact that satisfactory results are obtained for determination of thallium in this case indicate that the simultaneous presence of trivalent chromium will not interfere with the quantitative determination of thallium either.

As is evident from Table 2, determination of thallium as the dichromate in the presence of metals which are not precipitated by chromic oxide is possible, independently of the concentration of these metals. The limit of the permissible concentration of the accompanying metals is determined solely by the solubility of their salts in sulfuric acid solutions. This fact must be borne in mind particularly in the case of determination of thallium in the presence of those metals where this solubility is low, e.g., Sb^{III} [6] and Ge^{IV} [7].

Determination of Thallium in the Presence of Metals which form Sparingly Soluble Chromates

In order to establish the possibility of determining thallium quantitatively in the form of its dichromate

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*Cu^{II} and In^{III} are only precipitated by chromate from neutral solutions.

TABLE 2

Determination of Thallium in the Form of its Dichromate in the Presence of Zn, Cd, Fe, Al, Cu, Mg, Ni, Co, In, Ga, Ge, Sb, Tl^{III}

Taken, g/100 ml			Metals present as sulfates, g	Ratio Tl:Me	Tl found, g	Error, mg.
Tl	CrO_3	H_2SO_4				
0,0810	1	1	0,4 Zn	1:5	0,0810	0,0
0,0810	1	1	8,1 Zn	1:100	0,0808	—0,2
0,0405	3	1	8,1 Zn	1:200	0,0404	—0,1
0,0810	1	1	0,54 Cd	1:6,7	0,0808	—0,2
0,0810	1	1	8,1 Cd	1:100	0,0811	+0,1
0,0405	3	1	8,1 Cd	1:200	0,0405	0,0
0,0810	1	1	0,28 Fe^{III}	1:3,5	0,0810	0,0
0,0810	1	1	4 Fe^{III}	1:50	0,0810	0,0
0,0373	3	1	4 Fe^{III}	1:107	0,0372	—0,1
0,0810	2	2	0,37 Fe^{II}	1:4,6	0,0810	0,0
0,0810	1	10	0,16 Al	1:2	0,0809	—0,1
0,0810	1	1	2,4 Al	1:30	0,0808	—0,2
0,0373	3	1	2,4 Al	1:64	0,0373	0,0
0,0810	1	10	0,4 Cu^{II}	1:5	0,0810	0,0
0,0810	1	1	4 Cu^{II}	1:50	0,0810	0,0
0,0373	3	1	4 Cu^{II}	1:107	0,0371	– 0,2
0,0810	1	1	0,17 Mg	1:2	0,0810	0,0
0,0810	1	5	4,1 Mg	1:50	0,0808	—0,2
0,0405	1	1	4,1 Mg	1:100	0,0808	—0,2
0,0810	1	10	0,19 Ni	1:2,3	0,0810	0,0
0,0810	1	1	8,1 Ni	1:100	0,0810	0,0
0,0373	3	1	8,1 Ni	1:217	0,0370	—0,3
0,0810	1	10	0,19 Co	1:2,3	0,0808	—0,2
0,0810	1	1	6 Co	1:74	0,0809	—0,1
0,0373	3	1	6 Co	1:161	0,0373	0,0
0,0810	1	10	0,13 In	1:1,6	0,0808	—0,2
0,0810	1	10	0,1 Ga	1:1,2	0,0808	—0,2
0,0810	1	10	0,07 Ge	1:0,9	0,0808	—0,2
0,0810	1	10	0,02 Sb^{III}	1:0,2	0,0809	—0,1
0,0810	1	10	0,06 Tl^{III}	1:0,7	0,0810	0,0

*Mean of several determinations.

in the presence of Pb, Ag, Bi, Hg, and Ba which form sparingly soluble chromates, it is necessary to know the solubility of the chromates of these metals under the conditions used for precipitating $Tl_2Cr_2O_7$ [2]. The absence of such data in the literature made it necessary to find the maximum amounts of Pb, Ag, Bi, Hg, and Ba which are not precipitated in acid solutions by chromic oxide.

Results for the determination of thallium as its dichromate when the salts of the metals indicated are present separately are given in Table 4, while the results of such determinations when these metals are present simultaneously are given in Table 5.

The results obtained show that direct determination of thallium by the dichromate method is possible in acid solution in the presence of metals which form sparingly soluble chromates, but only in those cases where their concentrations do not exceed certain limiting values. At higher concentrations of these metals, results for thallium are on the high side because of coprecipitation of their chromates with thallium dichromate,.This error, as shown for the case of precipitation of thallium in the presence of silver (Table 4), can be cut down somewhat by decreasing the concentration of chromic oxide or by increasing the acid concentration. But, since a larger excess of chromic oxide is necessary [2] as the acid concentration is increased, the results for thallium depend on the ratio of acid and chromic oxide in solution.

TABLE 3

Determination of Thallium in the Form of Its Dichromate when Zn, Cd, Fe, Al, Cu, Ni, Co, In, Ga, and Ge are Present Simultaneously; 0.0810 g Tl, 7 g H_2SO_4, and 2 g CrO_3 taken per 100 ml of solution.

Metals present in the form of sulfates, g	Tl found, g*	Error, mg
$0,4Zn + 0,54Cd + 0,28Fe^{III} + +0,37Fe^{II} + 0,16Al + 0,4Cu^{II}$	0,0809	−0,1
$0,4Zn + 0,54Cd + 0,28Fe^{III} + + 0,37Fe^{II} + 0,16Al + 0,4Cu^{II} + + 0,19Ni + 0,19Co + 0,05\,In + + 0,03Ga + 0,07Ge$	0,0810	0,0

*Mean of several determinations.

TABLE 4

Determination of Thallium as its Dichromate in the Presence of Ba, Pb, Ag, Bi, and Hg

Taken, g/100 ml				Present, g (without water of crystallization)	Tl found, g*	Error, mg
Tl	CrO_3	H_2SO_4	HNO_3			
0,0767	1	—	10	0,8 $Ba(NO_3)_2$	0,0766	−0,1
0,0767	1	—	10	0,5 The same	0,0766	−0,1
0,0767	1	—	10	0,1 » »	0,0765	−0,2
0,0767	1	—	10	0,03 $Pb(NO_3)_2$	0,0786	+1,9
0,0767	1	—	10	0,02 The same	0,0766	−0,1
0,0767	1	—	10	0,01 » »	0,0765	−0,2
0,0810	0,35	1	—	0,02 $AgNO_3$	0,0865	+5,5
0,0810	0,35	1	—	0,01 The same	0,0810	0,0
0,0810	1	1	—	0,02 » »	0,0870	+6,0
0,0810	1	10	—	0,01 » »	0,0809	−0,1
0,0810	1	10	—	0,02 » »	0,0852	+4,2
0,0810	0,6	10	—	0,02 » »	0,0820	+1,0
0,0767	1	—	10	0,01 » »	0,0767	0,0
0,0810	1	10	—	0,03 $Bi(NO_3)_3$	0,0823	+1,3
0,0810	1	10	—	0,02 The same	0,0809	−0,1
0,0810	2,3	18	—	0,05 » »	0,0808	−0,2
0,0767	1	—	10	0,02 » »	0,0767	0,0
0,0767	1	—	10	0,01 » »	0,0766	−0,1
0,0810	1	10	—	0,08 $HgSO_4$	0,0814	+0,4
0,0810	1	10	—	0,05 The same	0,0810	0,0
0,0810	1	10	—	0,01 » »	0,0809	−0,1
0,0767	1	—	10	0,05 $Hg(NO_3)_2$	0,0766	−0,1
0,0767	1	—	10	0,005 $Hg_2(NO_3)_2$	0,0776	+0,9
0,0767	1	—	10	0,003 The same	0,0766	−0,1
0,0767	1	—	10	0,002 » »	0,0766	−0,1

*Mean of several determinations. The results indicate the permissible concentrations of the metals present.

TABLE 5

Determination of Thallium as its Dichromate in the Simultaneous Presence of Ag, Pb, Bi, Hg, and Ba

Taken, g/100 ml									Tl found, g*	Error, mg
Tl	H_2SO_4	HNO_3	$AgNO_3$	$Pb(NO_3)_2$	$Bi(NO_3)_3$	$Hg(NO_3)_2$	$HgSO_4$	$Ba(NO_3)_2$		
0,0767	—	10	0,01	0.02	0,02	0,05	—	—	0,0766	—0,1
0,0767	—	10	0,01	0,02	0,02	0,05	—	0,5	0,0766	—0,1
0,0810	10	—	0,01	—	0 02	—	0,05	—	0,0830	+2,0
0,0810	10	—	0,01	—	0,02	—	0,01	—	0,0823	+1,3
0,0810	10	—	0,01	—	0,02	—	—	—	0,0809	—0,1
0,0810	10	—	0,01	—	0,01	—	0,05	—	0,0810	0,0
0,0810	10	—	0,01	—	0.01	—	0,01	—	0,0809	—0,1

*Mean of several determinations.

TABLE 6

Determination of Thallium in the Presence of Metals Which Form, and Which do not Form, Sparingly Soluble Chromates

Simultaneously present, g*	Tl found, g	Error, mg
Sulfates Zn, Cd, Al, Cu^{II}, Fe^{III} 1 g ea. Co, Ni 0.5 g ea. In, Ga, Ge 0.1 g ea. Sb^{III} 0.5 g Nitrates: Ag, Bi, Hg^{II} 0.1 g ea.	0,0810 0.0809	0,0 —0,1

*Crystallization water is not included in the indicated amount of the salts present.

It is characteristic that the amount of bismuth nitrate which interferes with the direct determination of thallium (Table 4) is considerably less than that which is precipitated under similar conditions in the absence of thallium. In the latter instance the precipitate only appears after several days for a content of approximately 0.95 g of $Bi(NO_3)_3 \cdot 5H_2O$ in 100 ml of solution.

As is evident from Table 4, the permissible concentrations of the metals which form sparingly soluble chromates and which are present during the quantitative determination of thallium as its dichromate, change in the following order: Ba > Bi,Pb > Ag > Hg^{I}. This sequence is observed during precipitation of thallium dichromate from solutions containing 10 g of acid per 100 ml by chromic oxide, whose concentration amounts to 1 g in 100 ml of the liquid phase. Under these conditions the presence in 100 ml of solution of 0.05 g $HgSO_4$, 0.02 g $Bi(NO_3)_3$, 0.02 g $Pb(NO_3)_2$, 0.01 g $AgNO_3$, and 0.003 g $Hg_2(NO_3)_2$, does not interfere with thallium determination. The concentrations indicated are the maximum permissible values under the given conditions (Table 4).

Under similar conditions, $Ba(NO_3)_2$, apart from its dependence on the concentration, does not affect determination of thallium as its dichromate. The permissible concentration of this salt is determined, in the given instance, (Table 4), only by its solubility.

On changing the conditions for precipitating thallium dichromate, the limiting permissible concentration of metals which are precipitated by chromic oxide can change accordingly. Thus, the permissible concentration for bismuth nitrate can be increased if the thallium is determined under the conditions indicated in Table 4.

These concentration limits, of course, do not hold in the case of metals which form sparingly soluble chromates, when, under certain conditions, complexing agents are used which make it possible to keep the corresponding metals in solution.

It is characteristic that the simultaneous presence of Ag, Bi, Hg^{II}, Pb, and Ba in amounts which do not interfere with the determination of thallium as its dichromate when these metals are present separately, (Table 4) does not interfere with this determination in nitric acid solution either (Table 5). In sulfuric acid solutions, Ag and Bi in the same amounts do not interfere. However, the simultaneous presence of Ag, Bi, and Hg^{II} gives high results. At a much lower Bi concentration, or when Bi and Hg^{II} are present simultaneously, satisfactory results are obtained for the determination of thallium in the form of its dichromate in sulfuric acid solutions. (Table 5).

Determination of thallium as its dichromate in sulfuric acid solutions in the simultaneous presence of metals which form, and which do not form, sparingly soluble chromates, also give good results (Table 6).

These experiments show that the method for the quantitative determination of thallium in the form of its dichromate is, at the same time, a method which can be used for quantitative separation of thallium from accompanying elements. The fact that this complicated problem of separating thallium from other metals can be solved by a simple method involving readily available materials, means that the dichromate method for determination of thallium could be widely used for determining thallium with various combinations of elements.

Quantitative precipitation of thallium as its dichromate from acid solutions, combined with its quantitative separation from elements accompanying it, apart from its uses in analytical chemistry, may also be of interest for hydrometallurgical processes of thallium production [8], and, presumably, for preparing thallium compounds of high purity.

SUMMARY

It has been established that quantitative determination of thallium as its dichromate in acid solutions is, at the same time, a method for its quantitative separation from accompanying elements.

It has been shown that metals which do not form sparingly soluble chromates, in particular Zn, Cd, Al, Fe, Cu, Mg, Co, Ni, Sb, In, Ga, Ge, Tl^{III}, Cr^{III}, do not interfere with the determination of thallium as its dichromate.

Metals forming sparingly soluble chromates, such as Pb, Ag, Bi, and Hg, do not interfere with the determinations as long as the concentration of these elements does not exceed certain limiting values; barium does not interfere at any concentration.

It has been shown that thallium can be determined as its dichromate not only in sulfuric acid solutions, but also in solutions of other mineral acids, in particular, in nitric and perchloric acids. The permissible concentrations of these acids have been established.

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A METHOD FOR THE COMPLETE SPECTROGRAPHIC ANALYSIS OF MIXTURES OF THE OXIDES OF THE RARE EARTH ELEMENTS

R. R. Shvangiradze

Changes in chemical composition often essentially affect the kinetics of evaporation of samples and the excitation of the spectral lines. In order to standardize the evaporation process and the discharge, a foreign component is added in a large and always constant amount. The lines of the latter simultaneously serve as reference lines.

When the test mixtures consist of components with very close physicochemical properties, variations in the chemical composition should not affect the relative intensities of the spectral lines of the various elements. The relative intensities should change linearly with changes in relative concentrations. In such a case it should be possible to develop a method for the complete analysis of mixtures of various composition, without resorting to preliminary dilution of the samples several times.

The method consists essentially of the following. Standard samples of known but varying composition are prepared. To these standards are added all those elements which it is presumed will be present in the samples to be analyzed. By choosing as reference element one of the components which is always present in the test mixtures in known, though not constant amounts, it is possible to obtain constant calibration curves for each test component x_1 within the coordinates: $\log Ix_i/I_A - \log \alpha_1$. Here A is the element chosen as the reference element, $\alpha_1 = = 100\frac{C_{xi}}{C_A}$ is the concentration of the i'th test component with respect to element A in %. The linearity of the curves will demonstrate the independence of the relative intensities on the chemical composition. It is obvious that

$$C_{x_1} + C_{x_2} + C_{x_3} + \ldots + C_{x_i} = 100 - C_A;$$

then

$$\Sigma_{\alpha_i} = \alpha_1 + \alpha_2 + \alpha_3 + \ldots + \alpha_i = \frac{100\,(C_{x_1} + C_{x_2} + C_{x_3} + \ldots + C_{x_i})}{C_A} =$$

$$= \frac{100\,(100 - C_A)}{C_A}$$

or

$$\Sigma_{\alpha_i} - C_A + 100\,C_A = 10^4$$

and

$$C_A = 10^4/100 + \Sigma_{\alpha_i}. \tag{1}$$

Thus, by measuring the relative intensities of the chosen analytical pairs of spectral lines, and by determining by means of the calibration curves, the value of α for each component, it is possible by means of formula

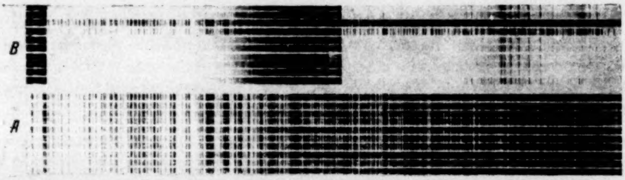
(1) to find the concentration of the element chosen as the reference element. Knowing the values of α_i and C_A, it is not difficult to establish the concentration of each component x_i of the mixture.

$$C_{x_i} = \alpha_i \cdot C_{A/100}. \tag{2}$$

The method presumes the existence of calibration curves for each component which is to be simultaneously determined in a mixture. During partial analysis, it is obvious that it is necessary to add the same component in known and invariably constant amounts.

Favorable conditions for developing a method for complete analysis exist in the case of mixtures of the oxides of the rare earths, the physicochemical properties of which are similar. As shown in a number of papers, the realtive intensities of the spectral lines of the various rare earths change very insignificantly, even for very sharp changes in excitation conditions and in the conditions for recording the spectra [1-5].

The independence of the relative intensities of the spectral lines of various rare earth elements on the chemical composition has been checked on mixtures of the oxides of the cerium subgroup. It has been experimentally established that the addition to any binary mixture of a third, fourth, etc., component, as well as changes in their concentration, even over very large limits, have almost no effect on the relative intensities of the lines of those components, the ratio of whose concentrations remains constant in the mixtures.



Scanning of the spectrum of rare earths with time during ignition in an arc. A) With graphite powder; B) without graphite powder.

The spectra were photographed on an ISP-51 spectrograph using a UF-84 camera. The oxides were mixed beforehand with graphite powder and ignited in a d.c. arc between carbon electrodes at a current strength of 5.5. amp.

The special part played by the graphite powder during evaporation of the non-conducting rare earth oxides in a d.c. arc should be noted. During ignition of oxides without graphite in the arc, the walls of the crater of the graphite anode are rapidly burnt, while on the anode there is formed a drop of the molten material, the temperature of which is not constant because of its ready access to atmospheric gases, and because of the difficulty of regulating the inter-electrode distance as a result of rapid changes in it. The intensity of the lines after the first 45-60 seconds is very low (the time of intense charring of the walls of the anode crater). After the crater has been completely destroyed, the rare earths start to evaporate, and their spectra appear. This process, however, does not last long; because there is no crater in the anode, the drop falls off.

After mixing the oxides with graphite the anode crater burns out considerably slower, and a high and comparatively stable temperature is established which ensures an almost constant intensity of the spectra during the time of complete burning of the sample. The reproducibility of the intensities essentially improves.

The spectrograms obtained during scanning of the arc radiation with time are shown in the diagram. The group of successive spectra designated by A relate to mixtures of the oxides with graphite powder in the proportion of 1:1, while the group designated by B relate to mixtures which do not contain graphite. During this scanning the casette was moved every 10 seconds.

As is evident from the diagram, mixing of the rare earth oxides with graphite powder is not only desirable, but essential. On mixing the oxides with graphite powder, the intensity of the cyanide bands which interfere drops essentially.

Ce, Nd, Sm, and Y are often present in appreciable amounts in rare earth concentrates isolated from ores and minerals. Accordingly, one of these elements is chosen as the reference element in individual cases.

In order to construct calibration curves, synthetic standards were prepared in which the concentration of the reference element varied from 10 to 70-90%, while the concentration of the test elements varied from 0.3-0.5 to 50-60%. The standards were diluted beforehand with graphite powder in the proportion of 1:9. Such a dilution essentially simplifies the spectra of the rare earths which are exceedingly rich in lines, a large number of weak lines disappear, and the most intense lines become suitable for analysis; the background in the spectra reduces almost to zero.

Calibration curves for analysis of mixtures of the cerium subgroup were constructed using Ce or Nd as reference element, while for the analysis of complex mixtures containing almost all the rare earths, the reference elements used were Sm or Y. All the curves obtained were linear; they can therefore be represented by a general formula of the type

$$\log \alpha_i = \log \alpha'_i + 1/\beta \, (\log I_{x_i}/I_A), \tag{3}$$

where α_i is the desired ratio of the concentration of the i'th component to the concentration of the reference element A (in %), α'_i is the same ratio when the intensities of the analytical line of the test element and that of the reference line are equal$-\log I_{x_i}/I_A = 0$, and β is the tangent of the angle formed by the straight line and the abscissa.

After determining the value of α_i from the calibration curves or from formula (3), the concentration of the reference element C_A can be determined by means of equation (1), while the concentration of each of the remaining elements can be determined by means of equation (2).

The analytical pairs of lines, the test concentration ranges, and the values of the parameters of the calibration curves α'_i and β for the analysis of various mixtures are given in Tables 1, 2, 3, and 4.

TABLE 1

Analysis of Mixtures of Ce-Subgroup Elements Using Ce as Reference Element

Test compound	Analytical pairs of lines	Test concentration range, %	α'	β
La_2O_3	La 3988,5/Ce 3984,6	0,5—15	5,7	0,97
Nd_2O_3	Nd 3951,2/Ce 3938,1	1,0- 40	12,5	0,89
Nd_2O_3	Nd 4446,4/Ce 4416,9	1,0—30	10,0	0,90
Sm_2O_3	Sm 4434,3 Ce 4416,9	0,5—10	4,9	0,96
Sm_2O_3	Sm 4478,6/Ce 4416,9	1,0—30	15,0	0,96
Sm_2O_3	Sm 3922,4/Ce 3895,1	2,0—40	24,0	0,94
Pr_6O_{11}	Pr 4056,5/Ce 4053,5	2,0—40	24,0	0,94

Knowing α'_i and β it is not difficult to reproduce a linear calibration curve. It should however, be pointed out that the lines can vary somewhat depending on experimental conditions and the apparatus used. Accordingly, in order to achieve high accuracy they should be determined on the basis of special standard samples.

The analytical results are reproduced with an accuracy of ± 2-4% relative, with the exception of analytical pairs of lines, in which samarium lines are present. In these cases the mean arithmetic error increases to ± 7-8%. The reason for this has been given before [6].

The complete analysis method was compared in actual practice with the method of adding a standardizing compound (internal standard), in particular CeO_2, to the samples [1,2].

TABLE 2

Analysis of Mixtures of Ce- Subgroup Elements using Nd as Reference Element

Test compound	Analytical pairs of lines	Test concentration range,%	α'	β
La_2O_3	La 4338,4/Nd 4235,2	0,5—20	5,9	0,96
La_2O_3	La 4238,4/Nd 4232,4	3,0—50	25,0	1,05
Pr_6O_{11}	Pr 4223,0/Nd 4235,0	0,5—20	6,3	0,99
Pr_6O_{11}	Pr 4223,0/Nd 4232,4	4,0—55	31,0	1,06
Sm_2O_3	Sm 4424,4/Nd 4456,0	0,5—20	7,5	0,96
Sm_2O_3	Sm 4434,3/Nd 4456,0	2,0—40	12,5	0,95

TABLE 3

Analysis of Mixtures of Rare Earth Oxides Using Sm as the Reference Element

Test compound	Analytical pairs of lines	Test concentration range, %	α'	β
La_2O_3	La 3938,5/Sm 3993,3	0,5—40	9,7	0,99
Pr_6O_{11}	Pr 4008,7/Sm 4006,6	1,0—40	11,0	0,97
Pr_6O_{11}	Pr 3908,0/Sm 3903,4	3,0—50	19,3	0,95
Nd_2O_3	Nd 4012,3/Sm 4006,6	0,5—40	3,9	0,94
Eu_2O_3	Eu 3930,5/Sm 3928,4	0,3—30	6,8	0,94
Gd_2O_3	Gd 4043,7/Sm 4068,3	1,0—50	40,0	0,98
Dy_2O_3	Dy 3899,5/Sm 3903,4	1,0—50	29,0	0,97
Dy_2O_3	Dy 3978,5/Sm 3970,5	0,5—40	29,0	0,97
Dy_2O_3	Dy 3944,7/Sm 3946,4	0,3—30	6,8	0,94
Ho_2O_3	Ho 4045,5/Sm 4041,7	0,5—40	5,5	1,01
Ho_2O_3	Ho 3891,0/Sm 3903,4	1,0—40	11,0	0,97
Er_2O_3	Er 3906,3/Sm 3903,4	3,0—50	70,0	0,92
Er_2O_3	Er 3506,3/Sm 3894,1	1,0—30	13,8	0,98
Tb_2O_3	Tb 3899,2/Sm 3903,4	1,0—40	23,5	0,95
Tu_2O_3	Tu 4242,2/Sm 4249,5	0,5—25	8,7	1,00
Y_2O_3	Y 3982,6/Sm 3970,3	0,3—30	8,7	0,33
Y_2O_3	Y 4039,8/Sm 4041,7	3,0—50	47,0	0,97

A comparison of the results obtained by both these methods for mixtures which had been subjected to chemical methods of separation, showed that the complete analysis method gives the higher accuracy. In the case of the method of adding a reference element, to the errors arising during the spectroanalytical process there is added the errors implicit in preliminary preparation of the samples for analysis. The most important sources of the latter kind of error are the calcination of both the test preparations and the internal standard to a constant weight, the difficulty of accurate weighing of small amounts and mixing them to give uniform distribution. Uniform distribution can only be reliably achieved by mixing the test sample with the internal standard in the form of solutions. These fairly difficult operations are automatically excluded when the complete analysis method is adopted. In addition, on adding a large amount of Ce to a sample, the spectrum becomes even more complicated, and it becomes necessary to use apparatus with a very high dispersion; on the other hand, dilution of the samples with graphite powder in the complete analysis method significantly simplifies the spectra of the test mixtures.

TABLE 4

Analysis of Mixtures of Rare Earth Oxides Using Y as the Reference Element

Test compound	Analytical pairs of lines	Test concentration range, %	α'	β
CeO_2	Ce 4222,6/Y 4251,2	1,0—30	20,0	1,00
La_2O_3	La 3988,5/Y 3951,6	0,3—10	2,0	1,16
La_2O_3	La 4238,4/Y 4224,3	0,3—10	1,8	1,15
Pr_6O_{11}	Pr 3908,0/Y 3930,1	0,5—15	4,0	1,15
Pr_6O_{11}	Pr 4423,0/Y 4224,3	0,3—10	2,0	1,30
Nd_2O_3	Nd 3951,2/Y 3951,6	0,5—20	9,5	1,04
Nd_2O_3	Nd 4012,2/Y 4039,8	1,0—30	20,0	1,00
Sm_2O_3	Sm 4434,3/Y 4443,6	0,5—20	6,0	1,00
Sm_2O_3	Sm 3963,0/Y 3951,6	1,0—30	13,0	1,08
Gd_2O_3	Gd 4262,1/Y 4251,2	2,5—40	34,0	1,15
Gd_2O_3	Gd 4327,1/Y 4357,7	0,3—15	6,5	0,95
Dy_2O_3	Dy 3931,5/Y 3930,1	0,5—20	9,6	0,96
Ho_2O_3	Ho 4254,4/Y 4251,2	1,0—30	42,0	0,97
Ho_2O_3	Ho 4254,4/Y 4224,3	0,3—10	6,8	7,02
Er_2O_3	Er 4008,0/Y 4039,8	2,5—50	100,0	0,90
Er_2O_3	Er 3906,3/Y 3930,1	2,0—10	14,4	0,90
Tb_2O_3	Tb 3899,2 Y 3957,6	1,0—30	10,5	0,93
Tb_2O_3	Tb 4326,5/Y 4357,7	0,3—10	2,9	1,03
Tu_2O_3	Tu 4242,2/Y 4251,2	1,0—25	21,0	0,96
Tu_2O_3	Tu 4242,2/Y 4224,3	0,2—10	2,9	1,02

SUMMARY

A method is suggested for the complete spectrographic analysis of mixtures containing commensurable concentrations of components whose physicochemical properties are similar.

During a comparison of the complete analysis method with the method in which an internal standard is added to the test mixture, it has been shown that in the case of mixtures of rare earth oxides the first technique gives more accurate results.

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THE ANALYTICAL CHEMISTRY OF THORIUM

COMMUNICATION 1. COMPLEXONOMETRIC DETERMINATION OF THORIUM IN MONAZITE CONCENTRATES

Yu.A.Chernikhov, V.F.Luk'yanov, and A.B.Kozlova

Of the titrimetric methods of determining thorium, prior to the introduction of complexons, there were only a few indirect methods [1-6] based on titration of the anion. These methods have disadvantages which are common to all indirect methods (the non-stoichiometric relation between cations and anions caused by formation of basic or acid salts, and by coprecipitation of foreign ions and by other causes). A more complete list of titrimetric and other methods for determining thorium can be found in reviews [7,8].

Complexonometric determination of thorium is a direct method, and is free from many of the disadvantages inherent in the indirect methods. In solution at pH about 3, thorium forms with Complexon III a soluble, colorless and stable complex with an instability constant of $10^{-23.2}$ [9]. In this compound one atom of thorium corresponds to one anion of Complexon III.

Alizarin S [11], chromazurol S [12], carminic acid [12], thoron [11], murexide [11], pyrocatechol violet [13], chromotrope 10 B, [9] etc. have been used as indicators for thorium.

During the determination of thorium in monazites, the most difficult and prolonged operation is the separation of thorium from rare earths and from phosphorus. For this purpose, wide use is made of methods based on precipitating thorium from strongly acid solutions. Under these conditions the solubilities of the corresponding compounds of thorium and the rare earths differ most from each other, while adsorption of foreign elements is reduced to a minimum. The method of extracting with mesityl oxide suggested by Leviene and Grimaldi [10] is very effective, since it is possible to separate thorium from most of the interfering elements in one operation, including separation from fluoride and phosphate ions. However, in addition to thorium, a considerable part of the uranium, vanadium, and zirconium is extracted and this requires additional purification.

Precipitation by the technique of "in situ nascendi" reagents is much better than the usual method in that the precipitates obtained by the former method are denser, more crystalline, and purer [14], while coprecipitation is considerably weaker. Diethyl or dimethyl oxalate is used for precipitating the oxalates of thorium and the rare earths. The following technique [15] has been suggested for precipitating thorium iodate by the method of "in situ nascendi" reagents. To the test solution is added a solution of potassium (or sodium) metaperiodate and ethylene glycol monoacetate $HO\text{-}CH_2\text{-}CH_2\text{-}OOC\text{-}CH_3$. The latter hydrolyzes to form ethylene glycol which reacts with periodate in an acid solution according to the equation:

$$HO-CH_2-CH_2-OH + HIO_4 \rightleftarrows 2HCHO + H_2O + HIO_3$$

Ethylene glycol monoacetate can be replaced by other reducing agents such as glycerol, saccharose, and ethylene glycol. It has been established that reduction of potassium periodate by glycerol is too rapid; this means that the precipitation reaction would not be slow enough, and, consequently, separation of thorium from the rare earths would not be so complete. On using saccharose, and also on adding ethylene glycol in small portions, the reaction proceeds slowly, and precipitation starts 3-5 minutes after addition of the reagent.

For determination of thorium in monazite concentrates, a method which is a combination of precipitation of the iodates and oxalates by the method of "in situ nascendi" reagents can be successfully used. This leads to the possibility of rapidly and completely separating thorium from elements which accompany it and interfere with its determination (rare earths, Zr, Fe, Ti, P, etc.).Using labeled atoms it has been established that during precipitation of the iodates by the method of "in situ nascendi" reagents, thorium is completely separated from the rare earths, and, in addition, from a considerable part of the phosphorus. Precipitation of the oxalates by the method of "in situ nascendi" reagents completely separates thorium from zirconium, titanium, iron, and phosphate ions. Such a method of separating thorium from accompanying elements makes it possible to use complexonometric titration.

TABLE 1

Indicator	pH of solution before titration	Complexon used, ml	Th, found, %
Uranon	2,40	12,75*	5,95
	2,40	12,80*	5,98
Alizarin S	2,50	12,65**	5,93
	2,50	12,65**	5,98
Pyrocatechol violet	2,50	12,60***	5,99
	2,50	12,60***	5,99

*Normality of the complexon with respect to thorium using uranon as indicator was 0.00467.

**Normality of the complexon with respect to thorium using alizarin S as indicator was 0.00473.

***Normality of the complexon with respect to thorium using pyrocatechol violet as indicator was 0.00475.

The reagent uranon (arsenazo)* is a good indicator for the complexonometric determination of thorium. In solutions with a pH of 2-4, uranon, which gives the solution a rose color, gives with thorium ions a lilac colored complex. During titration with Complexon III, the lilac color changes sharply to rose at the equivalence point. Uranon has the advantage over alizarin S, which has been suggested earlier, in that the color change has more contrast, and the influence of the rare earths on the endpoint is less pronounced(the rare earths tend to make the color change at the equivalence point more diffuse).

Pyrocatechol violet, which we synthesized according to Vodak's method [16] gave satisfactory results; however, the color change (from blue to yellow) during titration of thorium with complexon is not so sharp as when uranon is used as the indicator. The rare earths do not interfere during titration of thorium when pyrocatechol violet is used as indicator. Phosphate ions, even in small amounts interfere during titration of thorium whatever indicator is used.

Table 1 contains results for the determination of thorium in a sample of a monazite concentrate when all three indicators are used. The satisfactory agreement between the results means that any of these three indicators can be used, but, in view of its greater color change contrast, uranon is more convenient.

Determination of thorium in monazite concentrates. The test sample (20 g) was decomposed with sulfuric acid by the usual method [17]. After leaching out the sulfate with ice water (500-700 ml), the solution, without filtering it free from insoluble residue, was transferred to a 1 liter standard flask; after the solution had attained room temperature its volume was made up to the mark with water. Part of this solution was filtered for analysis, and 50 ml of it pipetted into a 600 ml bearer. To this solution was added 140 ml of potassium (or sodium) periodate solution containing 10 g of KIO_4, 40 ml of concentrated HNO_3, and 100 ml of H_2O (for each sample); to this solution was then added with stirring 50 ml of 12% saccharose solution (in two lots of 25 ml after an interval of 30 minutes). The precipitate was filtered through a filter (blue band) and washed 6-7 times with wash liquor containing 8 g of KIO_3, 100 ml of concentrated HNO_3, and 900 ml of H_2O. The precipitate was dissolved on the filter in hydrochloric acid (1:1) with sodium sulfite. The filter was washed several

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*For the synthesis of the indicator see J. Anal. Chem. 7, 231 (1952).

times with water (the volume should not exceed 75-100 ml). To the solution was added sodium sulfite (solid) until the solution was decolorized.

TABLE 2

Sample	Parallel aliquots	pH of solution before titration	Complexon used, ml	Th found in % by complexon method	Mean results, %	Deviation from the mean (absolute %)	Th found by gravimetric method, %	Mean result, %	Deviation from the mean (absolute %)
P-1	I	2,50	13,10	6,12		+0,06			
		2,50	12,95	6,05	6,06	−0,01	6,22	6,17	+0,05
		2,40	12,90	6,03		−0,03	6,12		−0,05
P-1	II	2,50	12,80	5,99	6,03	−0,04	6,11		+0,02
		2,50	13,00	6,07		+0,04	6,10	6,09	+0,01
							6,07		−0,02
H-1	I	2,50	15,12	7,06		+0,06			
		2,40	14,95	6,98	7,00	−0,02	6,93		−0,01
		2,40	14,90	6,96		−0,04	6,95	6,94	+0,01
H-1	II	2,50	15,12	7,06		+0,06	6,93		+0,03
		2,40	14,95	6,98	7,00	−0,02		6,90	
		2,40	14,90	6,96		−0,04	6,87		
									−0,03
H-2	I	2,50	15,20	7,10		+0,01	7,15		0,00
		2,50	15,20	7,10	7,09	+0,01	7,20	7,15	+0,05
		2,50	15,15	7,07		−0,02	7,10		−0,05
									−0,01
		2,50	15,15	7,07		−0,02	7,10		
H-2	II	2,50	15,20	7,10	7,09	+0,01	7,21	7,11	+0,10
		2,50	15,20	7,10		+0,01	7,03		−0,08
		2,50	15,75	7,35		−0,01	7,40		+0,04
O-1	I	2,50	15,80	7,38	7,36	+0,02	7,35	7,36	−0,01
		2,50	15,75	7,35		−0,01	7,32		−0,04
O-1	II	2,40	15,75	7,35		−0,01			
		2,50	15,75	7,35	7,36	−0,01	7,44	7,44	0,00
		2,40	15,80	7,38		+0,02	7,44		0,00
K-1	I	2,50	11,45	5,35		−0,01			
		2,50	11,50	5,37	5,36	+0,01	5,37	5,39	−0,02
		2,50	11,40	5,35		−0,01	5,41		+0,02
K-1	II	2,40	11,50	5,37		+0,01	5,42		+0,01
		2,55	11,50	5,37	5,36	+0,01	5,40	5,41	−0,01
		2,50	11,45	5,35		−0,01			

The solution was neutralized with ammonia (1:1) until a weak turbidity developed; 10 ml of concentrated HCl was added, followed by 100 ml H_2O and 7 g of dimethyl oxalate. The solution was heated, while stirring, to 60-70° on a hot plate, and after the solution had become turbid it was transferred to a warm sand bath. After not less than 30 minutes, 4 g of oxalic acid dissolved in 200 ml of water was added, and the whole left to stand for 1-2 hours (better still, overnight). The solution which had cooled to room temperature was filtered (blue band) and washed 6-7 times with a 2% oxalic acid solution containing 40 ml of concentrated HCl per liter. The precipitate was washed off the folded filter paper with hot water, and the filter washed several times with hot nitric acid and finally with water. The solution plus precipitate was evaporated to a small volume and 15-20 ml of aqua regia added. The solution was evaporated down to 5-10 ml and the operation repeated 2-3 times. The beaker was transferred onto the sand bath and 10 ml of perchloric acid added; the solution was then evaporated until the moist salts were formed. After cooling, 100 ml of water was added, and the pH of the solution adjusted with ammonia to 2.4-2.6 using α-dinitrophenol as indicator.

To the solution was added 1-2 drops of a 1% alcoholic solution of the indicator and the solution then neutralized by addition of ammonia (1:1) until a weak yellow color appeared; this color was then removed by addition of 1-2 drops of hydrochloric acid (1:1) (the pH can also be measured by means of a LP-5-meter). 5 drops of a 1% aqueous solution of uranon was added and the solution titrated with 0.03 M Complexon III until the lilac color changed to rose. The Complexon III is best standardized against an accurately prepared solution of thorium nitrate.

Table 2 contains the results for determination of thorium in a number of monazite concentrates from various deposits. For comparison, results obtained by the classical iodate method with a gravimetric finish are also included.

It is evident from these results that the complexonometric titration method is accurate enough; the error of the method is ± 0.04% absolute for thorium contents of 5-7%; in addition, this techinque permits the time taken for an analysis to be shortened apprecia bly.

SUMMARY

A method is suggested for the complexonometric titration of thorium in monazite concentrates, after separation of the thorium from accompanying elements by precipitating it in the form of the iodate and the oxalate by the method of "in situ nascendi" reagents. Thorium is titrated with Complexon III using uranon as indicator.

The method has been tried out on various samples of monazite concentrates. The accuracy of the method is 0.04% absolute for thorium contents of 5-7%.

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COPRECIPITATION OF ZIRCONIUM WITH TRIVALENT CERIUM OXALATE OBTAINED BY THE METHOD OF "IN SITU NASCENDI" REAGENTS

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For fractional precipitation of the oxalates of the rare earths, some authors [1-4] use dimethyl- and diethyl oxalates, which on heating gradually decompose to liberate $C_2O_4^{2-}$ ions. Zirconium often occurs in many of the rare earth minerals [5], so that in separating the rare earths the presence of zirconium must be taken into account. According to published data [6], zirconium gives complexes with four, six, or eight oxalate ions, formation of the first complex being accompanied by dissolution of the precipitate of $Zr(C_2O_4)_2$.

Trapping of zirconium may occur during precipitation of cerium oxalate as a result of coprecipitation. The aim of the work described here was to study the coprecipitation of zirconium with trivalent cerium oxalate obtained by the method of "in situ nascendi" reagents. A solution of anhydrous oxalic acid in absolute methanol [7] was used as a source of oxalate ions.

All experiments were carried out with the radioactive indicators Zr^{95} and Ce^{144}. Separation of the daughter element Nb^{95} from Zr^{96} was achieved as it accumulated by adsorption on MnO_2 from 10 N HNO_3 [8]. The radiometric purity of the indicators was checked by the method of Harley and Hallden [9]. The volume of solution was controlled by weighing on a microbalance. That part of the solution which remained on the precipitate after centrifuging and pouring off the liquid was also determined by weighing. The temperature was kept constant to within ± 0.05° by means of a water thermostat during the time of the experiments. Stirring was carried out with a mechanical stirrer operating at the rate of 450-500 revolutions/minute.

The amount of zirconium coprecipitated was determined from the change in activity of the liquid phase before and after precipitation; in a number of instances the activity of the solid phase was also measured, corrections being applied for the fact that the precipitate was moistened by solution.

TABLE 1

HNO_3, N	Solubility, g/100 g of solution	
	our results	Sarver's results
0,1	0,0130	—
0,25	0,0354	0,0355
0,5	0,1035	—
1,0	0,248	—
1,5	0,274	—
2,0	0,0703	0,6808

First of all, the solubility of cerium oxalate was determined at 25° in nitric acid solutions of varying concentration. The results obtained, in the main, coincide with results obtained by Sarver [10], who determined the solubility of oxalates in various acids by other methods.

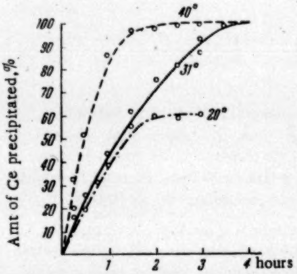
Since the solubility of cerium oxalate decreases with decreasing HNO_3 concentration, in order to ensure the most complete precipitation of cerium, the minimum concentration of HNO_3 was chosen which was still sufficient to prevent formation of colloidal particles capable of contaminating the precipitate [11]. Accordingly, in subsequent experiments, unless otherwise stated, cerium was precipitated in 0.15 N HNO_3.

In order to establish the optimum conditions for precipitating cerium with methyl oxalte, a series of experiments was carried out at 20, 30, and 40°. In these and subsequent experiments, a cerium nitrate solution containing 13.2 g/liter, and a solution of methyl oxalate (anhydrous $H_2C_2O_4$ in absolute CH_3OH) containing 135 g $C_2O_4^{2-}$ per liter were used.

The amount of methyl oxalate added in each experiment was 1 ml; cerium nitrate was added to the solution in the same amount, this corresponded to 25.61 mg of cerium oxalate. The total volume of solution in each experiment was 25 ml.

The curves obtained (diagram) show that the rate of precipitation of cerium oxalate, which is proportional to the rate at which the methyl oxalate decomposes, depends on the temperature and the time for which the solution is stirred. The nature of the curves indicate that precipitation is gradual and most uniform at 30°. Subsequent experiments were therefore carried out at 30°.

During studies of the nature of coprecipitation, all the experiments – with certain exceptions – were carried out at constant volume (25 ml), acidity (0.15 N HNO_3), and temperature (30°). The zirconium concentration of the solution was about 10-11 g/liter. The amount of methyl oxalate was four times the amount necessary for precipitating the cerium.



The experimental results (Table 2) show that on reprecipitating twice, a large part of the zirconium trapped in liberated, and only about 7% of the total amount remains in the precipitate; this shows that the coprecipitation is adsorptive in character.

The effect of the overcharge of the surface layer was studied by adding to a precipitate of cerium oxalate prepared beforehand, a zirconium solution (10-11 g/liter) and a saturated solution of cerium oxalate.

It follows form the results given in Table 3 that the order in which the solutions are added to the precipitate essentially affects the coprecipitation. The amount of zirconium coprecipitated increases significantly when zirconium is added to the cerium precipitate.

TABLE 2

Precipitation	Duration of stirring of solution, hr	Amt. of cerium oxalate ppt.		Amt. of zirconium coprecipitated, %
		mg	%	
Without recrystallization	3,5	25,35	98,9	57,3
	3,5	25,35	98,9	55,0
		Mean value		56,1
One reprecipitation	1,0	25,09	97,9	16.5
	1,0	25,09	97,9	20,4
		Mean value		18,5
Two reprecipitations	1.0	24,83	96,9	4.2
	1,0	24,80	96.9	8,8
		Mean value		7,0

In all probability, on direct addition of a zirconium solution to a negatively charged precipitate of $Ce_2(C_2O_4)_3$, there occurs adsorption of positive complex Zr ions [12]. Subsequent addition of Ce^{3+} ions leads, apparently, to replacement of only some of these ions. When the solutions are poured together in the reverse order, it is mainly Ce^{3+} ions that are adsorbed.

Precipitation under conditions where there was insufficient precipitant, from solutions in which the cerium concentration was increased five times, showed that coprecipitation of zirconium decreases, and reaches a value of about 5%. These results again confirm our hypothesis regarding the mechanism of coprecipitation.

It is clear from Table 4 that the amount of zirconium coprecipitated decreases with increasing HNO_3 concentration. This could be the result of changes in the surface of the $Ce_2(C_2O_4)_3$ as a consequence of an increase in solubility, or as a result of competition between hydrogen ions and zirconium ions in the secondary adsorption layer.

TABLE 3

Order in which the solutions are added to the cerium oxalate ppt.	Time of stirring	Amt. of zirconium coprecipitated, %
Zirconium solution added to a saturated solution of cerium oxalate	0,5	7,6
	2,5	7,2
Saturated solution of cerium oxalate added to zirconium solution	2,5	32,5
	3,5	38,3

TABLE 4

HNO_3 concentration	Zr coprecipitated, %
0,1	56,1
0,2	47,6
0,3	41,0
0,4	33,9

Note. Duration of stirring 3.5 hr.

A study of the effect of the zirconium concentration on its coprecipitation with cerium oxalate was carried out using the same conditions as before; in individual experiments, the only solutions used were ones with different concentrations of zirconium, obtained by mixing Zr^{95} and the same compounds of the stable isotope of zirconium.

The results given in Table 5 show that the amount of zirconium coprecipitated increases with its increasing concentration in solution, but the percentage of the zirconium thereby trapped decreases.

TABLE 5

Zr concentration g/liter	Duration of stirring, hours	Amt. of coprecipitation		Zr concentration g/liter	Duration of stirring hours	Amt. of coprecipitation	
		Cerium oxalate, %	Zirconium, %			Cerium oxalate %	Zirconium, %
$5{,}0 \cdot 10^{-4}$	1,0	42,9	27,5	$7{,}0 \cdot 10^{-3}$	2,5	81,5	37,1
$5{,}0 \cdot 10^{-4}$	1,5	61,2	38,5	$7{,}0 \cdot 10^{-3}$	3,5	99,0	35,5
$5{,}0 \cdot 10^{-4}$	2,5	81,5	64,0	1,2	1,0	42,9	4,6
$5{,}0 \cdot 10^{-4}$	3,5	99,0	60,1	1,2	1,5	61,2	4,7
$7{,}0 \cdot 10^{-3}$	1,0	42,9	36,6	1,2	2,5	81,5	5,5
$7{,}0 \cdot 10^{-3}$	1,5	61,2	37,7	1,2	3,5	99,0	5,3

SUMMARY

It has been established that zirconium is coprecipitated with trivalent cerium oxalate as a result of adsorption; coprecipitation of zirconium decreases with increasing acidity of the medium. With increasing zirconium concentration in solution, its adsorption increases, but the percentage of it trapped decreases.

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DETERMINATION OF ZIRCONIUM BY MEANS OF N-BENZOYLPHENYLHYDROXYLAMINE

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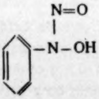
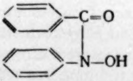
In recent years, for the determination of zirconium and for its separation from other elements, wide use has been made of organic reagents including cupferron [1-6] and its analog N-benzoylphenylhydroxylamine (BPHA), which has been recommended as an analytical reagent for the precipitation of metals by Bamberger [7].



Cupferron



N-Benzoylphenylhydroxylamine

Schome [8-10] used BPHA for determination of titanium, aluminum, and copper by a gravimetric method, and vanadium by a photometric method. He showed that BPHA differs from cupferron in its stability to the effect of heat and light. Ryan and Lutwik [11] used BPHA for determining tin. Moshier and Schwarberg [12] and Majumdar and Mukhejee [13] used this reagent for determining tantalum. Sina [14] used BPHA for determining molybdenum, while Dyrssen [15] used it for extracting lanthanum, thorium, and uranium.

The aim of the work described here was to establish more accurately the conditions for determining zirconium by means of benzoylphenylhydroxylamine, both in pure salts and in the presence of other elements, and also to try to separate in this way, zirconium from tantalum, niobium, and certain other elements.

EXPERIMENTAL

N-Benzoylphenylhydroxylamine was synthesized by Schome's method [8]. The product was recrystallized from ethanol (or from hot water). The reagent is obtained in the form of white, needle-like crystals (m.p.121°), which are sparingly soluble in cold water [at room temperature (25°) the solubility is about 0.5 g liter] and readily soluble in hot water, alkali solutions, ethanol, diethyl ether, chloroform, and cyclohexanone. The reagent is completely stable in a solution of sulfuric or hydrochloric acid; only in a strongly alkaline medium, after several days, is there observed any decomposition.

For our experiments we used a solution of zirconium hydroxide which was standardized gravimetrically.

In order to establish the optimum conditions for precipitating zirconium with BPHA, we studied the relation between completeness of precipitation of zirconium and the amount of BPHA. For this purpose various amounts of BPHA dissolved in 40 ml of boiling water was added to 60 ml of a standard solution of a zirconium salt (0.0152 g ZrO_2) (total volume 100 ml, HCl concentration 0.15 N). Solution plus precipitate was heated on a boiling water bath for 10-15 minutes, the whole being stirred occasionally. In this way the compound formed between zirconium and benzoylphenylhydroxylamine which separated out, was precipitated as a white precipitate which readily coagulated. After this stage, on cooling of the solution, the precipitate was filtered through a fine filter paper, washed with a solution of 1% hydrochloric acid containing 0.05% BPHA, then it was dried and calcined in a porcelain crucible at 1000-1100° to constant weight. The results obtained are shown in Fig. 1. It should be noted that, from a practical point of view, it is better to add excess reagent for more complete precipitation, particularly in a strongly acid medium .

In order to establish the effect of acidity on completeness of precipitation of zirconium, the latter was precipitated with BPHA for different concentration of the acid in solution. The results are given in Fig. 2.

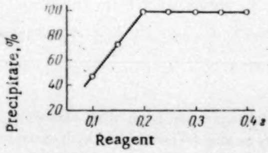


Fig.1. Relation between completeness of precipitation of zirconium and the amount of BPHA.

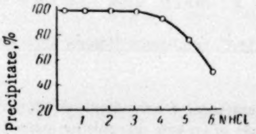


Fig.2. Effect of HCl concentration on completeness of precipitation of zirconium with N-benzoylphenylhydroxylamine.

We also studied the effect of various mineral acids and of tartaric acid on precipitation of zirconium. For this purpose, various amounts of hydrochloric, sulfuric, or tartartic acid solutions were added to a solution containing zirconium, the solutions were diluted to 150 ml and 0.4-0.5 g of BPHA dissolved in 100 ml of boiling water added. Solution plus precipitate was heated for 15-20 minutes on a boiling water bath; the solution was stirred occasionally. The precipitate was then filtered immediately through a fine filter paper, since zirconium benzoylphenylhydroxylaminate is almost insoluble in hot water. The precipitate was washed with 1% hydrochloric acid solution containing 0.05% BPHA, and was then dried and calcined in a porcelain crucible at 1000-1100°. The results obtained are given in Table 1.

In order to establish the effect of hydrogen peroxide, which is used for preventing precipitation of titanium niobium, and vanadium, on completeness of precipitation of zirconium, to 150 ml of solution containing zirconium, to 150 ml of solution containing zirconium was added about 1 ml of 30% hydrogen peroxide, after which the zirconium was precipitated with a solution of BPHA as described above. The precipitate was filtered off, calcined, and weighed. The experimental results, which are given in Table 1, show that hydrogen peroxide does not affect completeness of precipitation of zirconium. It should be noted that in the presence of hydrogen peroxide, it is best to heat the solution plus precipitate on a gently boiling water bath for not more than 15 minutes.

Next, we studied the precipitation of zirconium in the presence of other elements. For this purpose, standard solutions of iron, aluminum, chromium, titanium, niobium, tantalum and rare earth salts were used. Zirconium was precipitated and determined as described above. The experimental results are given in Table 2.

In order to determine its composition, zirconium benzoylphenylhydroxylaminate was prepared as follows. To a solution containing zirconium hydroxylaminate was added different amounts of hydrochloric acid and 0.5-1.5 g of BPHA dissolved in 50-100 ml of boiling water (total volume 100-150 ml). Solution plus precipitate was heated on a boiling water bath for 30 minutes, and, without cooling, the precipitate was filtered through a glass crucible; the precipitate was washed with a hot 1% solution of hydrochloric acid containing 0.05% BPHA, and several times with hot distilled water; it was finally washed with 30 ml of ether (BPHA itself is soluble in ether but zirconium benzoylphenylhydroxylaminate is not) and dried at 105-110° to constant weight. After this, some of the precipitate was placed in a porcelain crucible and calcined at 1000-1100° to constant weight, and weighed as ZrO_2. The results obtained, which are shown in Table 3, show that the composition of the precipitate isolated from the hydrochloric acid solution corresponds to the formula $Zr(BPHA)_4$.

Zirconium benzoylphenylhydroxylaminate $Zr(BPHA)_4$ can be used as a gravimetric form.

In order to establish the stability of zirconium benzoylphenylhydroxylaminate to temperature, a thermogravic analysis was carried out. It follows from Fig. 3 that the precipitate is stable up to a temperature of 240°. In order to get the gravimetric form ZrO_2 it is sufficient to calcine the hydroxylaminate at 500°.

TABLE 1

ZrO_2, g		Error, g	Medium
taken	found		
0,0303	0,0303	±0,0000	2,4 *N* HCl
0,0303	0,0304	±0,0001	
0,0152	0,0151	−0,0001	
0,0152	0,0153	+0,0001	
0,0062	0,0062	±0,0000	
0,0062	0,0062	±0,0000	
0,0062	0,0062	±0,0000	
0,0016	0,0016	±0,0000	
0,0016	0,0017	+0,0001	
0,0031	0,0031	±0,0000	2,4 *N* HCl and 5% $C_4H_6O_6$
0,0031	0,0030	−0,0001	
0,0031	0,0031	+0,0000	2,4 *N* HCl and 0,15% H_2O_2
0,0031	0,0033	+0,0002	
0,0152	0,0151	−0,0001	2,4 *N* HCl (95°)
0,0152	0,0150	−0,0002	
0,0152	0,0153	+0,0001	3,6 *N* H_2SO_4
0,0062	0,0064	+0,0002	
0,0152	0,0154	+0,0002	3,6 *N* H_2SO_4 and 5% $C_4H_6O_6$
0,0062	0,0062	±0,0000	
0,0152	0,0152	±0,0000	3,6 *N* H_2SO_4 and 0,15% H_2O_2
0,0062	0,0062	±0,0000	

TABLE 2*

Oxides of other metals added, g		ZrO_2 found, g	Error, g	Oxides of other metals added, g		ZrO_2 found, g	Error, g
Fe_2O_3	0,033	0,0032	+0,0001	Cr_2O_3	0,020	0,0031	±0,0000
"	0,033	0,0031	±0,0000	BPHA	0,020	0,0031	±0,0000
Al_2O_3	0,150	0,0033	+0,0002	Zr:BPHA	0,010	0,0030	−0,0001
"	0,150	0,0030	−0,0001	BPHA	0,020	0,0029	−0,0002
TiO_2	0,018	0,0031	±0,0000	$(Nb, Ta)_2O_5$	0,010	0,0030	−0,0001
"	0,018	0,0033	+0,0002	BPHA	0,010	0,0030	−0,0001

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* (0,0031 g ZrO_2 taken)

TABLE 3

Zirconium benzoylphenylhydroxylaminate ppt wt, g	Found, g		Zr:BPHA	HCl concentration, N
	Zr	BPHA		
0,1170	0,0119	0,1051	1 : 3,8	0,15
0,1168	0,0119	0,1049	1 : 3.8	0,15
0,1170	0,0119	0,1051	1 : 3,8	1,0
0,1150	0,0119	0,1031	1 : 3,7	1,0
0,1169	0,0119	0,1050	1 : 3,8	2,3
0,0554	0,0053	0,0501	1 : 4,0	3,1
0,0951	0,0091	0,0860	1 : 4,0	4,2
0,0940	0,0093	0,0847	1 : 4,0	5.3
0,0958	0,0094	0,0864	1 : 4,0	6,0

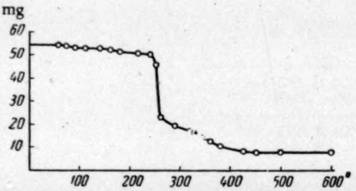

Fig. 3. Thermolysis curve for zirconium benzoylphenylhydroxylaminate.

SUMMARY

A new method has been developed for the quantitative precipitation of zirconium with N-benzoylphenylhydroxylamine.

A study has been made of the effect of various mineral acids, tartaric acid, and hydrogen peroxide on the completeness of precipitation of zirconium with N-benzoylphenylhydroxylamine.

Precipitation of zirconium in the presence of other elements has been investigated, and it has been shown that zirconium can be separated from iron, aluminum, chromium, titanium, niobium, and tantalum.

The composition of zirconium benzoylphenylhydroxylaminate has been determined: the composition of the precipitate which separates out of hydrochloric acid solutions corresponds to the formula Zr(BPHA)$_4$.

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A NEW PHOTOMETRIC METHOD FOR THE DETERMINATION OF VANADIUM

G. V. Rabovskii, T. F. Kuznetsova, and V. A. Belonogova

The oxidation of quinquevalent vanadium in a sulfuric acid medium by phenylanthranilic acid, or by the salts of diphenylaminesulfonic acid, is a reaction which possesses a high sensitivity, and permits detection of 0.2 γ of vanadium in 1 ml of solution. Despite such a high sensitivity it has not found application for the photometric determination of vanadium because of the low stability of the colored products formed, and the comparatively rapid change from one color to the other [1,2]. We cannot agree with this, however, since, according to our observations, the stability of the indicator color depends on the acidity of the medium. In solutions containing 5 M/liter and more of sulfuric acid, the color appears immediately, and it is stable long enough for its optical density to be measured.

It is clear from Table 1 that the optical density of colored solutions, for the same vanadium concentration, does not change in the course of 30 minutes. It drops slightly after 60 minutes. However, even in this case, the difference in optical densities for adjacent concentrations of vanadium remains the same as that which is observed when measurements of the optical density are made 30 minutes after adding the indicator. The calibration curve is displaced parallel to the curve obtained when values of the optical density measured 5-10 minutes (diagram) after addition of the indicator are used. Accordingly, it should be possible to determine the vanadium concentration on the basis of the differences in the optical density of the colored solutions and a standard [3] even when the measurements are made one hour after preparing the solution.

TABLE 1

Relation between Optical Density and the Time after which Measurements of Optical Density Are Made. (H_2SO_4 concentration 5M/liter, total volume of solution 50 ml, FEK-M colorimeter, green filter)

Amount of V, mg	Value of the optical density				
	Immed.	After 5 min	After 10 min	After 30 min	After 60 min
0,02	0,072	0,700	0,072	0,071	0,062
0,04	0,145	0,145	0,145	0,140	0,132
0,06	0,215	0,214	0,215	0,210	0,202
0,08	0,286	0,285	0,285	0,280	0,272
0,10	0,354	0,352	0,353	0,348	0,338

The amount of indicator added to the solution is very important. For vanadium concentrations of 0.01 to 0.1 mg in 50 ml of solution, it is essential to add 1.5-2.0 ml of a 0.02% solution of barium diphenylaminesulfonate, or 8-12 drops of a 0.1% solution of phenylanthranilic acid.

Colored ions such as iron, uranium, trivalent chromium, etc., do not interfere with the determination of vanadium (Table 2).

When the test material is dissolved, quadrivalent vanadium may be present in addition to quinquevalent vanadium. Potassium permanganate is usually used to oxidize the quadri- to the quinquevalent form. When this technique is adopted in the cold, if trivalent chromium should be present, it is not oxidized to the sexivalent form. Accordingly, the basic problem is to reduce excess potassium permanganate without touching the quinquevalent vanadium.

Sodium nitrite was used for removing excess permanganate, since nitrous acid in a weakly acid medium does not reduce VO_2^+ because of the nearness of their oxidation – reduction potentials [4]. If 0.05 M sodium nitrite is carefully added until the permanganate is decolorized, and one drop of nitrite added in excess, and then urea added immediately, the quinquevalent vanadium is not reduced to the quadrivalent state even in 3-4 N sulfuric acid.

TABLE 2

Effect of Colored Ions on the Value of the Optical Density during Vanadium Determination (Green filter)

Amt of V, mg/50 ml of solution	Added							
	0	Fe 100 mg			U 100 mg			Cr 3 mg
		I	II	III	I	II	III	
0,02	0,070	0,070	0,069	0,068	0,072	0,069	0,070	0,067
0,04	0,139	0,143	0,138	0,140	0,148	0,141	0,141	0,140
0,06	0,210	0,213	0,208	0,210	0,219	0,210	0,215	0,211
0,08	0,280	0,280	0,278	0,281	0,290	0,285	0,285	0,281
0,10	0,351	0,352	0,348	0,351	0,360	0,350	0,355	0,349

TABLE 3

Determination of Vanadium in Steels

Standard sample	Content, %			V determined, %	Relative error, %
	V	Cr	Ni		
	0,290	0,890	3,940	0,292	+0,69
	0,290	0,890	3,940	0,289	—0,34
	0,290	0,890	3,940	0,287	—1,06
30 c	0,290	0,890	3,940	0,288	—0,69
	0,290	0,290	3,940	0,290	—0,00
	0,290	0,890	3,940	0,292	+0,69
	0,240	—	—	0,226	—5,8
	0,240	—	—	0,228	—5,0
	0,240	—	—	0,228	—5,0
	0,240	—	—	0,228	—5,0
30 b	0,240	—	—	0,228	—5,0
	0,240	—	—	0,226	—5,8
	2,26	12,55		2,35	+3,9
	2,26	12,55		2,27	+0,44
87	2,26	12,55		2,25	—0,44
	2,26	12,55		2,35	+3,9
	2,26	12,55		2,27	+0,44
	2,26	12,55		2,27	+0,44

Procedure for vanadium determination. An aliquot of test material containing 0.1-1.0 mg of vanadium is dissolved in 30 ml of aqua regia and the solution evaporated with 20 ml of H_2SO_4 (1:1) until SO_3 fumes appear. 20-30 ml of water is added, followed by 1-2 drops of hydrogen peroxide (to reduce sexivalent chromium) and the mixture heated to the boil. The insoluble residue is filtered off and washed several times with hot water.

The filtrate and wash liquors are collected in a 100 ml standard flask and their volume made up to the mark with water. 10 ml of this solution is transferred into a 50 ml beaker; 0.1 N $KMnO_4$ is added dropwise until the pink color does not disappear for 5 minutes. Excess permanganate is removed by careful dropwise addition of 0.05 M sodium nitrite, one drop of the latter is added in excess, and 0.5 g of urea added. The solution is transferred to a 50 ml standard flask, and 5 ml of H_3PO_4 (4:1), added; the solution is then made almost up to the mark with H_2SO_4 (1:1)*, finally, 8-10 drops of 0.1% phenylanthranilic acid is added. The solution is

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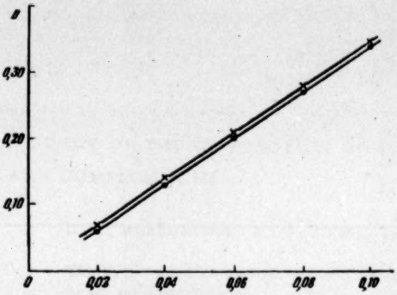
* H_2SO_4 (1:1) and H_3PO_4 (1:1) should be given preliminary treatment with K MnO_4, sodium nitrite, and urea.



Amt. of V in mg

×) Optical density measured after 5 minutes; ●) ditto after 60 minutes.

made up to the mark with H_2SO_4 (1:1), the solution is thoroughly shaken up, and, after 5 minutes, the optical density is measured on a FEK-M apparatus in a No.4 cuvette using a green filter.

The zero solution is prepared by taking 10 ml of the test solution, treating it as described above but omitting addition of the indicator.

Table 3 contains results for the determination of vanadium in standard samples of steel.

It is clear from these results that the suggested photometric method of determining vanadium is no less accurate than existing methods, while it is much quicker to carry out than these others since it does not require removal of colored ions.

SUMMARY

A photometric method has been developed for the determination of vanadium which is based on oxidation of phenylanthranilic acid or of diphenylaminesulfonic acid salts by quinquevalent vanadium.

Iron, uranium, trivalent chromium, and nickel ions do not interfere with the determination of vanadium.

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A STUDY OF THE INTERACTION OF SEXIVALENT URANIUM AND COMPLEXON III

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A number of reviews have been published on the application of complexons in analytical chemistry [1-7]. However, there is very little information regarding the interaction of uranium ions and Complexon III. Brintzinger and Hesse [8] have isolated a compound with the composition $(UO_2)_2H_2(C_{10}H_{12}N_2O_8)\cdot H_2O$. Cabell [9] has established potentiometrically that on adding Complexon III to a solution of uranyl nitrate, the following reactions may occur:

$$UO_2^{2+} + H_2\gamma^{2-} \rightarrow UO_2H\gamma^- + H^+ \,*$$

$$2UO_2^{2+} + H_2\gamma^{2-} \rightarrow (UO_2)_2\gamma,$$

in which the first equation is characteristic for solutions with a ratio of $C_{Complexon}/C_U \geq 1$, while the second equation is characteristic for solutions with a ratio of $C_{Complexon}/C_U = 0.5$. Liberation of hydrogen ions during the interaction of uranium with Complexon III, coupled with an increase in pH at the beginning of precipitation of the diuranate, indicate a complex forming process. The author concluded that compounds of uranium with Complexon III exist in the range pH 3-5.

In order to establish the properties and the nature of the compound of uranium with Complexon III we made use of a number of physicochemical methods, and also of a preparative method.

Ion Exchange Method. Ion exchange is widely used not only for separating elements, but also as a method for studying the state of ions in solution [10]. We have studied the relation between the sorption of uranium from solutions containing Complexon III and the pH, and also between this sorption and the concentration of the ion being coordinated. In order to keep the pH of the solution passing through the ion exchange resin constant, the sorbent in the column was brought into equilibrium with the test solution. The cation exchange resin KU-2 and the anion exchange resin EDE-10**, prepared according to GOST 5629-52 were used for the work.

The solution containing uranium and Complexon III in a definite ratio at various pH values was passed through the sorbent layer at the rate of 0.8 cm/minute. Uranium was determined photometrically in the filtrate by means of peroxide (anion exchange resins), or in the desorbed sulfuric acid solution vanadometrically (cation exchange resins).

On the basis of the curves obtained (Fig. 1) a number of conclusions can be drawn.

1. Uranium forms with ethylenediaminetetracetic acid, under certain conditions, complex compounds of an anionic type which are sorbed on an anion exchange resin, and pass through a column packed with a cation exchange resin.

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* γ stands for the anion of ethylenediaminetetracetic acid.

**The particle size of the sorbent was 0.25 mm; the parameters of the column were h = 28 cm; D = 1 cm; the volume of sorbent for each test (swollen state) was 10 ml.

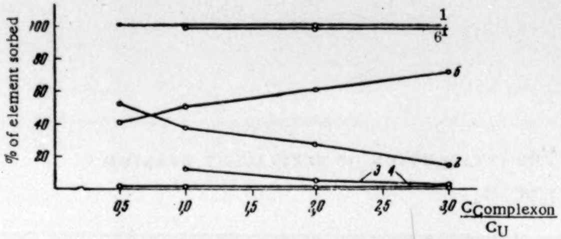

Fig. 1. Relation between sorption of uranium and the ratio $C_{Complexon}/C_U$. 1) pH 1.7 (cation exchange resin KU-2), 2) pH 5.5 (cation exchange resin KU-2), 3) pH 8.0 (cation exchange resin KU-2), 4) pH 1.7 (anion exchange resin EDE-10), 5) pH 5.5 (anion exchange resin EDE-10), 6) pH 8.0 (anion exchange resin EDE-10).

2. The extent to which complex formation takes place depends on the hydrogen ion concentration; in acid solutions (pH 1.7), 100% sorption of uranium is observed in the presence of ethylenediaminetetracetic acid on a cation exchange resin, while it is hardly sorbed at all on an anion exchange resin. At pH 5.5 the uranium is partly bound as an anionic complex, since part of the uranium is held not only by the cation exchange resin but also by the anion exchange resin. Further pH increases lead to increased concentration of the anionic form.

These results are in agreement with those of Macek and Pribil [11] which were obtained during a study of complex formation of uranium by electrophoresis on paper.

3. The compound of uranium and Complexon III possesses low stability, since on increasing the concentration of the ion being coordinated (at constant pH) sorption of uranium on the cation exchange resin decreases while it increases on the anion exchange resin.

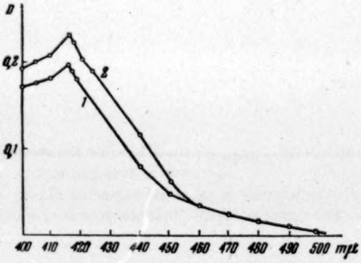

Fig. 2. Absorption curves for uranyl nitrate at pH 1.45 (1) and pH 3.2 (2).

Spectrophotometric method. The optical density of the test solutions was measured on a Beckman spectrophotometer fitted with glass cuvettes having a path for the light beam of 10.00 mm; measurements were made at room temperature in the range 400-600 mμ. A strictly constant slit width was established for each wavelength. The reproducibility of the optical density measurements was approximately 0.001-0.005 units.

It is known [12-13] that the absorption bands of an aqueous solution of uranyl nitrate are located in the visible part of the spectrum in the range 400-500 mμ, while those of Complexon III are located in the infrared and ultraviolet regions [14-16].

As our experiments showed, 0.01-0.1 M solutions of Complexon III[*] at pH 1.5-7.0 have a zero value for the optical density in the range 400-500 mμ.

From the absorption curves for 0.02 M solutions of uranyl nitrate in 0.1 M potassium chloride solution (Fig. 2), it is clear that the absorption maximum of the solution is found at 416 mμ[**], while the optical density depends on the hydrogen ion concentration. The latter is connected with the formation of uranyl hydroxy complexes [13], the absorption bands of which in the visible part of the spectrum are found almost in the same place. There is a published reference to the fact that at pH 0.1-1.55 the dominating ions is UO_2^{2+}, while at higher pH values, ions with a complex composition are formed [12-13].

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[*] Commercial Complexon III was reprecipitated three times according to a technique described in [17].

[**] We do not regard this value as an absolute value, since the scale of the apparatus was not accurately set; we have based our conclusions only on the relative changes in this value.

A comparison of the absorption curves of an aqueous 0.02 M solution of uranyl nitrate, and a solution of the same concentration containing 0.01 M Complexon III, at pH 1.4-1.5, shows (Fig. 3), that on adding Complexon III to the test solution, the nature of the curve does not change; only an increase in the optical density is observed.

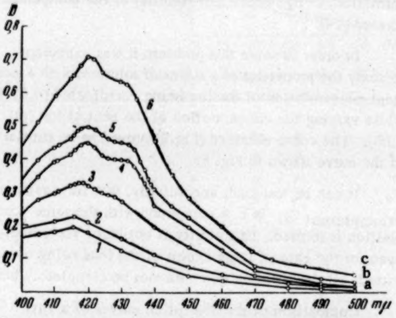

Fig. 3. Absorption curves: 1) Uranyl nitrate (pH 1.45);
2) solution with $C_{Complexon}/C_U$ ratio = 0.5 (pH 1.5);
3) " " " " " = 0.5 (pH 2.4);
4) " " " " " = 0.5 (pH 3.5);
5) " " " " " = 0.5 (pH 3.9);
6) " " " " " = 0.5 (pH 5.1).

An increase in the pH of the original solution also causes a clear (from 416 to 420 mμ) shift in the maximum on the curve; this testifies to the formation of a new chemical compound in solution. It might be assumed that favorable conditions for obtaining this compound are created at pH> 3, since at lower pH values the form of the curve is not clear, this in all probability being connected with dissociation of the compound formed.

The change in the value of the optical density as a function of the pH of the medium for a ratio of $C_{Complexon}/C_U = 0.5$ is shown in Fig.4.

The slow initial rise in the curve (up to pH 4) coupled with the absence of a clear switch over to a horizontal part, can apparently be explained by the formation of a strongly dissociated compound. At pH > 4, hydrolysis is probably superimposed on the complex formation process.

Similar experiments were carried out with solutions in which the ratio of $C_{Complexon}/CU=1$.

In Fig. 5 are shown absorption curves for a solution which was 0.02 M with respect to uranyl nitrate and Complexon III for various pH values.

Addition to an uranyl nitrate solution of an equimolar amount of Complexon III increases the optical density of the solution, but at pH ≤ 3.8 the nature of the absorption curve does not change. With increasing acidity the optical density (at 436 mμ) increases, it achieves a maximum value at pH 5.5, remains constant to pH 5.9, and then, starting at pH 6, drops again (Fig. 4).

At pH 3.8-6.0 displacement of the absorption maximum to the longer wavelength side (436-437 mμ) is observed.

The experimental results indicate that the stability of the complex compound is highest at pH 4.9-5.5, since at pH > 6 the absorption curves exhibit a poorly defined maximum at 436 mμ, while at pH 3.8 the extent of complex formation is considerably weaker.

The absorption curves for solutions which are 0.02 M with respect to uranyl nitrate and 0.04 M with respect to Complexon III are identical to the absorption curves for a ratio of $C_{Complexon}/Cu = 1$ (Fig. 6). The only difference is that the optical density of the solutions is higher, while the maximum (437 mμ) on the curves is expressed more clearly. The curves relating optical density to pH are similar to those obtained for the ratio $C_{Complexon}/C_U = 1$ (Fig. 4).

On increasing the ratio $C_{Complexon}/C_U$ further, the nature of the curves does not change, but the value of the optical density increases all the time. In Fig. 7 are shown the absorption curves for ratios of $C_{Complexon}/C_U = 2.3$, and 4 (pH 5.7-5.8).

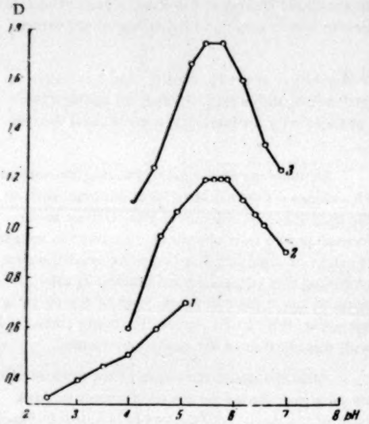

Fig.4. Relation between the optical density of the solution and pH: 1) At a ratio of $C_{Complexon}/C_U = 0.5$; 2) At a ratio of $C_{Complexon}/C_U = 1$; 3) At a ratio of $C_{Complexon}/C_U = 2$.

In Fig. 8 is shown the relation between the optical density of the solution (at 438 mμ) and the concentration of the ion being coordinated (for a constant value of the pH of 5.85). In all these experiments the concentration of the solution with respect to uranyl nitrate was 0.01 M, while the concentration with respect to Complexon III was changed from 0.01 to 0.06 M. In Fig. 8 we restricted ourselves to the final point obtained for a ratio of $C_{Complexon}/C_U = 6$. However, the value of the optical density increased even at ratios of $C_{Complexon}/C_U > 6$. The latter might be caused either by stepwise complex formation, or by insufficient stability of the compound formed [18].

In order to solve this problem it was expedient to study the properties of a series of solutions with a constant concentration of the ion being coordinated (0.01 M) while varying the concentration of the central ion (pH 5.85). The curve obtained (Fig.9) proved to be similar to the curve shown in Fig. 8.

It can be assumed, accordingly, that for a ratio of $C_{Complexon}/C_U \geq 1$, a compound with the same composition is formed. Its stability is not high; accordingly, even for the case of large excess of the ions being coordinated, all the uranium taken cannot be completely bound.

Comparison of the absorption curves of uranyl nitrate and Complexon III at pH 1.4-1.5 gives a basis for assuming that a complex compound is not formed under these conditions.

Conductometric method. Conductometric titration of 0.0084 M uranyl nitrate with 0.1 and 0.05 M Complexon III solutions was carried out by means of a Wheatstone bridge, a resistance box KMS-6 being used as three arms of the bridge. The frequency used was 1000 cycles. The null instrument was a galvanometer with a shadow pointer M 91/A with a sensitivity of about $5 \cdot 10^{-8}$ amp per scale division. The a.c. current was rectified with a germanium rectifier. The resistance of the solution was measured to an accuracy of the third place. Titration was carried out at 25 ± 0.01° in a vessel with electrodes made from platinized platinum. The cell constant was equal to 0.64. Corrections for dilution of the solution during the titration were applied in each experiment. On the curves $1/R_x - C_{Complexon}/C_U$ (Fig. 10) there is a clearly expressed break at a ratio of $C_{Complexon}/C_U = 0.5$, which suggests that a chemical compound is formed at this point.

Our results agree with the results of Hara and West [19], obtained by the method of high frequency titration. These authors consider that at pH 3.5-4.0 ethylenediaminetetracetic acid reacts with uranium to form a stable compound at a ratio of $C_{Complexon}/C_U = 0.5$.

Preparative method. It is known [17] that the salts of ethylenediaminetetracetic acid are sparingly soluble in many organic solvents. A mixture of alcohol and acetone in the proportion of 2:1 by volume proved to be the most suitable for separating the compound of uranium with Complexon III. The compound was isolated under conditions where there was a deficiency and an excess of Complexon respectively, with respect to the uranium.

To 15 ml of an aqueous suspension of ethylenediaminetetracetic acid (183.5 mg) was added with stirring a solution of ammonia until the former dissolved completely; a known amount of uranyl chloride (299 mg uranium) was then added and the pH adjusted to 4. The solution was allowed to stand for 10-15 minutes, after which a mixture of 60 ml of methanol and 30 ml of acetone was added to it. A yellow precipitate separated out on standing. After 10 minutes the precipitate was filtered on a Buchner funnel under vacuum; it was washed with 50 ml of methanol and then with 50 ml of acetone, and, finally, with 50 ml of ether. The compound obtained was allowed to dry in air for two days. We shall call this compound material A while we shall call the

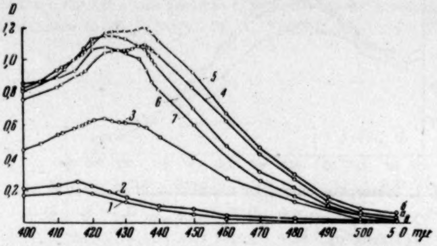

Fig. 5. Absorption curves. 1) Uranyl nitrate solution (pH 1.45) ;
2) Solution with a ratio of $C_{Complexon}/C_U$ = 1 (pH 1.5);
3) " " " " " 3.8);
4) " " " " 4.9);
5) " " " " " 5.5);
6) " " " " " 6.4);
7) " " " " " 7.0).

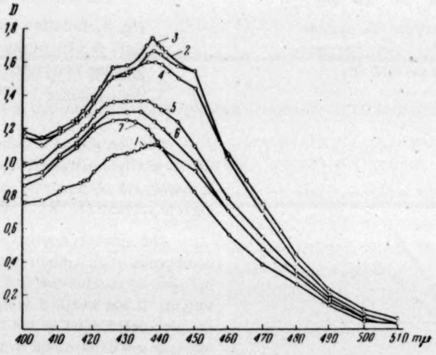

Fig. 6. Absorption curves for solutions with a ratio of $C_{Complexon}/C_U$ = 2 for various pH values. 1) pH 4.1; 2) pH 5.2; 3) pH 5.85; 4) pH 6.2; 5) pH 6.6; 6) pH 6.9; 7) pH 7.1.

next material which we prepared material B. The method used for preparing material B was substantially the same as that used for preparing material A, the essential difference being that material B was isolated from a solution with pH 5.5 when there was excess ethylenediaminetetracetic acid present as compared to uranium, (299 mg of uranium and 734 mg of the acid). It should be pointed out that material B separated out more completely from solution than material A.

Preliminary experiments showed that at pH 4-5.5, from a solution containing either uranyl nitrate or ethylenediaminetetracetic acid (their concentrations remained the same as before) alone, a precipitate does not form on addition of methanol and acetone.

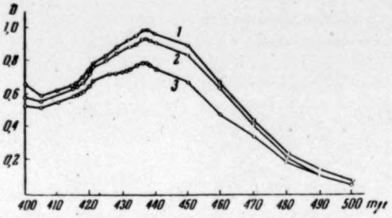

Fig. 7. Absorption curves for solutions with pH 5.7-5.8; 1) $C_{Complexon}/C_U = 4$; 2) $C_{Complexon}/C_U = 3$; 3) $C_{Complexon}/C_U = 2$.

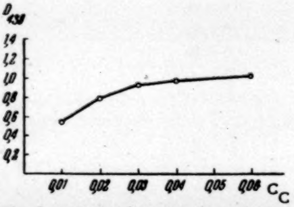

Fig. 8. Relation between the optical density of the solution and Complexon III concentration at pH 5.85 (C_U = = const.).

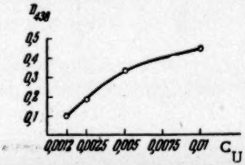

Fig. 9. Relation between the optical density of the solution and uranium concentration at pH 5.85 ($C_{Complexon}$ = const).

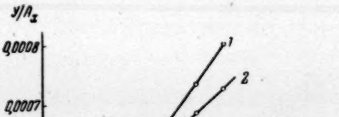

Fig. 10. Conductometric titration curves for a solution of uranyl nitrate (pH 3.5) titrated with Complexon III.

The compounds obtained were in the form of a fine crystalline material, light yellow in color, which is readily soluble in water and is almost insoluble in organic solvents (alcohol, ether, acetone, etc).

The uranium content was determined by careful combustion of an aliquot of the material in a crucible, followed by calcination in a muffle at 900° to constant weight. It was weighed as U_3O_8. Water of crystallization was determined by the hydride method, while total nitrogen was determined by the Dumas method.

Since the compound of uranium with Complexon III is decomposed by the action of excess ammonia with liberation of ammonium diuranate and free Complexon III, the latter can be determined by the usual method [17]. For this purpose 40 mg of each of the materials (A and B) was dissolved in 10 ml of water and excess (about 20 ml) of 12.5 N ammonia free from carbonates added; the solution was thoroughly agitated and allowed to stand for 15-20 minutes. A precipitate of ammonium diuranate separated out with time; this was filtered off and washed with a buffer mixture (in the presence of which the titration is carried out) and the filtrate obtained titrated with a standard solution of magnesium chloride in the presence of acid chrome dark blue.

The composition of the material A was found to approximate to the empirical formula $(UO_2)_2\gamma \cdot 3H_2O$, while that of material B was close to $(NH_4)_2(UO_2\gamma) \cdot 3H_2O$. Table 1 contains the means of the results for a number of determinations.

TABLE 1

Compound	Calculated, %					Found, %				
	U	H_2O	N_{tot}	γ	$\frac{\gamma}{U}$	U	H_2O	N_{tot}	γ	$\frac{\gamma}{U}$
$UO_2)_2\ \gamma \cdot 3H_2O$	54,18	6,11	3,17	32,0	0,59	53,83	5,4	3,8	25,0	0,46
$NH_4)_2|UO_2\gamma| \cdot 3H_2O$	36,74	8,33	8,64	44,4	1,21	35,94	7,67	87,0	46,0	1,28

The molar electrical conductivity [20] of 0.001 M aqueous solutions of compounds A and B was 52 and 209 $ohm^{-1}\ cm^2$ respectively.

There are published references [21] to the fact that compounds which break down into two ions* give electrical conductivity values of about 100 $ohm^{-1}cm^2$, while those which break down into three ions give electrical conductivity values of about 250 $ohm^{-1}cm^2$; on this basis, it can be concluded that in aqueous solution material B dissociates into three ions, while material A dissociates only to a very small extent.

SUMMARY

Ion exchange, spectrophotometric, and conductometric techniques have been used to study the interaction of uranyl ions with Complexon III in solution.

It has been established that uranyl forms a complex compound with Complexon III at pH > 3.

It is suggested that, depending on the ratio of the concentration of Complexon III and uranium in solution, two compounds are formed with molar ratios of complexon : uranium of 1 and 0.5.

It has been found that the complex compounds of uranium with Complexon III exhibit low stability; it increases in the pH range 3-8.

Two compounds of uranium with Complexon III have been isolated, and it has been established that their compositions approximate to the formulas $(UO_2)_2\nu \cdot 3H_2O$ and $(NH_4)_2(UO_2\nu) \cdot 3H_2O$.

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**In Russian.

MICROTITRATION OF RHODIUM WITH SODIUM PIPERIDINEDITHIOCARBAMATE

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The complex chlorides of the platinum metals give colored products* with $SnCl_2$ in hydrochloric acid solutions. Formation of these colored products is used as the basis for a considerable number of photometric methods of determining the platinum metals [1-4]. The colored products formed are readily extracted by organic oxygen-containing solvents [1,5]. The composition of the compounds has not been studied in detail and has not been established hitherto. An exception is Pt, the mechanism of whose interaction with $SnCl_2$ has been the subject of a large number of papers. Some authors [2,9,10] have assumed that the development of the color is connected with the conversion of platinum into a lower valence state. Others [5,6,12] consider that the yellow color develops as a result of liberation of platinum metal to form a stable colloid. Recently, some authors [7,8] have advanced the opinion that the color is determined by formation of a complex cation which contains both tin and platinum metal. The formula $[PtSn_4Cl_4]Cl_4$ has been ascribed to the product obtained by the reduction of platinum with $SnCl_2$. In 1938 Pollard suggested titrating the colored compounds of platinum [9,11] and palladium [10] with $SnCl_2$ or $SnBr_2$ with sodium diethyldithiocarbamate. In this way it is possible to determine from 0.001 to 1.0 mg of platinum or palladium/ml [10]. Pollard [10] tried to determine rhodium by titration with sodium diethyldithiocarbamate after addition of concentrated $SnBr_2$ solution. The solution of the complex chloride of rhodium contained 0.05 mg Rh/ml. In contrast to platinum and palladium, after addition of $SnBr_2$ the rhodium solution was heated, since only on heating does the color which is characteristic for rhodium develop. It was observed that 0.0005 mg rhodium/ml gives a weak color. When greater amounts of rhodium were present (0.05 mg/ml), although a color developed, the compound which was formed on titrating with sodium diethyldithiocarbamate was not completely extracted with benzene. Increasing the amount of rhodium and carbamate did not improve the results.

The work described here was carried out in order to establish the possibility of titrating rhodium with a carbamate having a higher molecular weight. Since there are very few methods for determination of small amounts of rhodium, while there are only four methods for its volumetric determination, we thought it would be interesting to develop a method for the titrimetric determination of rhodium.

On titrating rhodium with diethyldithiocarbamate, we found that on adding a solution of the latter to the red solution obtained on heating the complex chloride of rhodium with $SnCl_2$, a yellow turbidity appears which is not extracted by benzene; as a result, titration is impossible. The explanation for the fact that rhodium, in contrast to platinum and palladium, is not titrated with sodium diethyldithiocarbamate, is presumably the following: The product formed by the interaction of rhodium with $SnCl_2$ combines with sodium diethyldithiocarbamate; however, the reaction is very much slower than is the case during titration of platinum and palladium. During titration, part of the sodium diethyldithiocarbamate manages to decompose, since the reaction is carried out in strongly acid medium, and this reagent decomposes readily under the influence of acids. Moreover, the compound obtained is sparingly soluble in benzene, in contrast to the analogous compounds of platinum and palladium.

On the basis of these considerations, the titration conditions were modified; the acid concentration and the amount of $SnCl_2$ were lowered and the duration of heating cut; in addition, a suitable solvent was chosen for the compound formed. Despite the modifications adopted, satisfactory results were not obtained on titrating with sodium diethyldithiocarbamate. Accordingly, we tried to modify not only the titration conditions, but also to choose as titrant a carbamate which is more stable to the action of acids.

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*A similar reaction occurs when $SnBr_2$ is used, but in this case Pd is reduced to the metal.

Experiments on precipitation of rhodium and platinum from solutions of their complex chlorides by means of sodium diethyl- and piperidinedithiocarbamate confirmed the opinion of Gleu and Schwab [13] that the latter reagent is more stable to the effect of acids. Accordingly, we assumed that this reagent would be more convenient for titrating rhodium.

Preliminary experiments showed that sodium piperidinedithiocarbamate is a more suitable reagent for rhodium determination. Because of the low solubility of the compound of rhodium with sodium piperidinedithiocarbamate in benzene, it was necessary, in order to extract this compound, to choose a more suitable solvent. An attempt was made to replace benzene by chloroform and dichloroethane. It was found that the precipitate only partially dissolves in chloroform, and has a tendency to collect at the interface between the aqueous and chloroform layers; the compound dissolves completely in dichloroethane forming an orange colored solution.

Good results were only obtained when the hydrochloric acid concentration of the solution was between 0.7 and 1.2 N during the titration.

0.003 to 0.3 mg of rhodium can be titrated in 3 ml of the solution to be titrated (or 0.001-0.1 mg/ml). It is best to prepare the solutions so that the amount of reagent used for titration is approximately equal to the amount of rhodium and does not exceed 1 ml. Thus, in order to determine 0.003-0.015- mg, 0.015-0.075 mg, and 0.075- 0.30 mg of Rh it is necessary to use solutions containing 0.08 mg/ml, 0.4 mg/ml, and 2.0 mg/ml of reagent respectively.

It is not convenient to titrate small amounts of rhodium since, under such conditions, a weak color obtained by the interaction of rhodium with $SnCl_2$ is observed, and it is difficult to establish the endpoint. Titration of rhodium in amounts greater than that indicated above is impossible, since a large amount of precipitate is obtained which does not dissolve completely in the dichloroethane and partly collects at the interface.

NaCl in amounts of 0.1 to 0.5 mg/ml does not affect the titration results.

As a result of this preliminary work the following technique is suggested for determination of rhodium in a solution of its complex chloride.

Technique. The solution of the complex chloride of rhodium (0.003-0.3 mg Rh) is placed in a small beaker which is placed on a water bath, excess hydrochloric acid is removed by evaporating the solution 3-4 times to dryness, the residue being dissolved up each time in hot water. 1 ml of aqueous NaCl containing 0.3 mg/ml is placed in the beaker beforehand in order to prevent hydrolysis.

The dry residue is finally washed with 2.5 ml of 0.90 N hydrochloric acid into a test tube with a ground glass stopper (diameter of stopper 20 mm, length 110 mm); to the solution is added 0.5 ml of 1 M $SnCl_2$ in 0.90 N HCl and the whole heated by placing the test tube in a beaker of boiling water for 10 minutes; it is then cooled and 10 ml of dichloroethane added; the solution is finally titrated with an aqueous solution of sodium piperidinedithiocarbamate of the appropriate concentration.

The sodium piperidinedithiocarbamate solution is added gradually in small aliquots (0.05-0.1 ml), the test tube being stoppered after addition of each aliquot and vigorously shaken (10-15 times) so that the precipitate which is formed in the form of a yellow turbidity in the aqueous layer is completely transferred into the dichloroethane layer.

The titration end point is that point at which the aqueous layer becomes colorless; it is established by comparing the aqueous layer with a test tube filled with water against a white background.

The sodium piperidinedithiocarbamate solution is standardized against a solution of rhodium of known strength. The $SnCl_2$ solution should be clear. In order to get such a clear solution, after the $SnCl_2$ has been dissolved the solution is allowed to stand for several hours, after which it is filtered free from hydrolysis products. A solution prepared in this way is suitable for use for 5-6 days.

All the platinum metals interfere with the titration. A fresh solution of carbamate which has not stood for more than 5-6 days should be used for titration.

TABLE 1

Rhodium taken		Reagent used, ml	Rhodium found, mg	Absolute error, mg	Error, %	Notes
ml	mg					
0,70	0,3120	0,42	0,3120	±0,0000	0,0	Rhodium concentration 0.445 mg/ml Reagent concentration 20 mg/ml
0,60	0,2670	0.35	0,2590	−0,0080	2,9	
0,40	0,1780	0,25	0,1870	+0,0090	5,1	
0,20	0,0890	0,12	0,0890	±0,0000	0,0	
1,00	0,0890	0,60	0,0890	±0,0000	0,0	Rhodium concentration 0.089 mg/ml Reagent concentration 4.0 mg/ml
0,80	0,0712	0,48	0,0712	±0,0000	0,0	
0.60	0,0534	0,36	0,0534	+0,0000	0,0	
0,40	0,0356	0,23	0.0351	−0,0005	1,4	
0,20	0,0178	0,12	0,0178	±0,0000	0,0	
1,00	0,0178	0,61	0,0181	+0,0003	1,7	Rhodium concentration 0.0178 mg/ml Reagent concentration 0.8 mg/ml
0,70	0,0125	0,41	0,0122	−0,0003	2,4	
0,60	0,0108	0,36	0,0107	−0,0001	0,9	
0,40	0,0072	0,25	0,0074	+0,0002	2,8	
0,20	0.0036	0,12	0,0036	±0,0000	0,0	
0,15	0,0027	0,08	0,0024	−0,0003	11,1	

Results of determinations of rhodium by means of sodium piperidinedithiocarbamate are given in Table 1.

On titrating platinum and palladium with sodium piperidinedithiocarbamate, results were obtained which were similar to those obtained by Pollard on titrating with sodium diethyldithiocarbamate. Titration of platinum and palladium with sodium piperidinedithiocarbamate does not increase the sensitivity of a determination as compared with determination of Pt and Pd with sodium diethyldithiocarbamate.

SUMMARY

A method is described for the determination of small amounts of rhodium (0.003-0.3 mg) in solutions of its complex chlorides; it is based on extraction titration with sodium piperidinedithiocarbamate of the red colored interaction product of Rh and $SnCl_2$.

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DETERMINATION OF FREE SULFUR BY ITS REDUCTION TO HYDROGEN SULFIDE

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The two most widely used methods at the moment for the determination of free sulfur are the sulfite and cyanide methods. The sulfite method [1] gives good results when the test material contains relatively large amounts of free sulfur. For sulfur contents below 0.05% its determination becomes difficult. The cyanide method is usually used for small amounts [2-7]. There are other methods [8-11].

During sulfate determination by reduction of the sulfate to hydrogen sulfide by means of divalent tin and phosphoric acid, we noticed that, simultaneously, as an intermediate product, elemental sulfur is formed [12]. Since the iodometric determination of hydrogen sulfide is very accurate, it was of interest to establish the possibility of reducing free sulfur to H_2S by the method indicated, so that the iodometric finish could be used. For this purpose a solution of chemically pure sulfur in acetone was prepared, known amounts of this solution were then taken by means of an accurate pipet, and, after careful removal of the acetone on a gently boiling water bath, the sulfur was determined as indicated previously [12]. Quantitative results were, however, not obtained when such a technique was adopted. The reason for this is that on heating above 100° the vapors which are liberated take some of the free sulfur which has not yet been reduced to H_2S with them this sulfur is then deposited on the walls of the apparatus used for reduction and is not returned to the sphere of the reaction. Obviously, the small amounts of elemental sulfur which are formed as an intermediate product during reduction of sulfates,on account of their high dispersivity, and apparently amorphous state, react very rapidly to be converted into hydrogen sulfide, while sulfur in the form of even very fine crystals is reduced more slowly to H_2S and is partially carried off by the liberated vapors. Thus, determination of elemental sulfur by direct reduction to hydrogen sulfide with divalent tin and phosphoric acid is impossible.

In order to make such a method possible, it is necessary, after extracting the sulfur with acetone, to choose conditions which will ensure its rapid conversion to sulfate with subsequent reduction of the latter to H_2S.

Kiba, Akaza, and Sugishita [13] while determining sulfur in thiosulfate and thiocyanate by reduction with divalent tin and phosphoric acid, also established that it is necessary to oxidize the sulfur of the compounds indicated into sulfate.

A solution of chemically pure sulfur in acetone containing 0.205 mg of S per ml was prepared. An accurately measured aliquot of this solution was pipetted into a 50 ml beaker, and the acetone carefully removed (without boiling it) on a heated water bath. In order to oxidize the free sulfur to sulfate the dry residue was treated in the beaker with a solution of bromine in CCl_4 and nitric acid. After removal of the nitric acid by evaporating with hydrochloric acid, the contents of the beaker were transferred into a quartz holder in which the reduction was to be carried out; some potassium chloride was added and the whole evaporated to dryness on a water bath and the reduction then carried out as described previously [12].

As the results given in Table 1 show , oxidation of elemental sulfur to sulfate with subsequent reduction of the latter to hydrogen sulfide is quantitative. This method was accordingly used for determination of free sulfur in some samples of natural sulfur-containing materials.

An aliquot of rock weighed out on an analytical balance was placed in a paper thimble which was then placed inside the case of a Chervyakov extraction apparatus. Free sulfur was extracted with acetone for not less than 16 hours. The acetone extract was transferred to a 50 ml standard flask and the volume made up to the mark with acetone.

Since the sulfur-containing rock often contains gypsum (Middle Volga) the possibility is not excluded that very small particles of gypsum may get into the acetone extract. Accordingly, it is advisable to allow the acetone solution to stand in the standard flask for some time and an aliquot carefully pipetted out. The aliquot was transferred into a small beaker and evaporated to dryness on a heated water bath. The procedure subsequently adopted for preparing the solution and for carrying out the determination is described below. The presence of free sulfur in the first four samples was established beforehand by the sulfite method.

TABLE 1

Sulfur, mg			Sulfur, mg		
taken	found	error	taken	found	error
5,12	5,08	—0,04	1,02	0,98	- 0.04
5,12	5,10	—0,02	0,41	0,39	—0,02
2,05	2,03	—0,02	0,41	0,41	±0,00
2,05	2,04	—0,01	0,10	0,11	+0,01
1,02	0,98	—0,04	0,10	0,12	+0,02

TABLE 2

Test material	Sulfur found, %	
	by the classical method	by reduction to H_2S
Sulfur-containing calcite (Middle Volga)	3,08*	3,10
Sulfurized ash tuff (Kamchatka)	1,98*	1,99
Sulfur-containing rock (Kara-Kum)	0,87*	0,85
Sulfur-containing rock (Kara-Kum)	0,094*	0,09
Black silt (Black Sea)	0,10**	0,10
Grey silt (Black Sea)	0,06**	0,06
The same	0,05**	0,05

*Sulfite method

**Gravimetric method

Determination of free sulfur in samples of sea silt was carried out on the residue left after treating the test sample with dilute hydrochloric acid on heating in a current of CO_2, and with subsequent filtration for removal of sulfides and sulfates as described before [4]. The residue left after filtration was placed in a desiccator and the free sulfur extracted with acetone. In parallel, the free sulfur was also determined gravimetrically in the same samples on another aliquot of their acetone extracts.

As is evident from Table 2, the results are fully satisfactory.

On the basis of the research carried out, the following analytical procedure can be recommended.

An aliquot of test material placed in a paper thimble was introduced into the sleeve of a Chervyakov extraction apparatus. The thimble was covered with a small filter paper with a broken tip in order to prevent possible splashing when the condensate drips from the condenser.

During analysis of materials containing sulfide and sulfate sulfur in addition to free sulfur (various silts-sea, estuary, lake) the sulfide and sulfate should be removed beforehand by treating with dilute HCl in a stream of CO_2 on heating, as described by Ostroumov [4].

The sample placed in the thimble of the extraction apparatus was covered with acetone which had been dried and redistilled beforehand, and more acetone added so that the whole was drained down into the flask; the sample was then extracted with acetone on a gently boiling water bath for not less than 16 hours. Where it was necessary to interrupt the extraction, it was essential to make sure that the paper thimble containing the sample was kept covered with acetone in order to protect the material from oxidation. When extraction was complete, the acetone solution was transferred to a standard 50 ml flask, after removing excess acetone by evaporation; the volume was made up to the mark with acetone. The acetone solution was left to stand, and an aliquot part taken without disturbing the small amount of precipitate which was sometimes present; the aliquot was pipetted into a 50 ml beaker. Beaker plus acetone solution were placed on a heated water bath and the solution carefully evaporated to dryness without letting the acetone boil.

The free sulfur was oxidized to sulfate by Allen and Bishop's method [14]. To do this the beaker was removed from the bath and allowed to cool; the residue, after removal of the acetone, was treated with 2-3 ml of a solution of bromine in CCl_4 (2 parts Br_2 and 3 parts CCl_4 by volume); the beaker was covered with a watch glass and was left at room temperature for 10-15 minutes (during this time it was given an occasional swirl). 5 ml of concentrated nitric acid was added and the beaker and its contents allowed to stand for a 10-15 minutes further. Without removing the watch glass, the beaker was then placed on a closed, water bath, and carefully heated to remove most of the bromine. The watch glass was removed, the beaker was then placed in one of the holes in the water bath and its contents evaporated to dryness.

In order to remove the nitric acid completely the dry residue in the beaker was treated with 3 ml of HCl and again evaporated to dryness. Not more than 0.1 g of KCl (chemically pure) was added to the beaker on the tip of a spatula for facilitating subsequent reduction, another 3 ml of HCl was added, and again the contents of the beaker were evaporated to dryness. The dry residue was treated with a few drops of hydrochloric acid and heated on a water bath, the contents of the beaker were then transferred into the holder of the reduction apparatus, and bottom and walls of the beaker were washed with hot water from a washer. The holder of the apparatus was placed in one of the holes on the water bath and the contents evaporated to dryness.

To the dry residue in the holder was added 8 ml of reducing mixture (to the mark on the holder), and the holder placed in the reducing apparatus which had been filled beforehand with CO_2; CO_2 was bubbled through the apparatus for a further 4-5 minutes and heating then started. The temperature was gradually taken up to 300° and the apparatus kept at this temperature for 25-30 minutes for complete reduction of sulfate to hydrogen sulfide as described before [12].

The liberated hydrogen sulfide was absorbed with cadmium acetate solution. When reduction was complete the suspension of cadmium sulfide obtained was poured into an acidified 0.01 N I_2 solution. Excess iodine was titrated with 0.01 N $Na_2S_2O_3$ solution.

1 ml of 0.01 N I_2 is equivalent to 0.00016 g S.

In conclusion, I should like to thank E. A. Ostroumov for his valuable advice.

SUMMARY

A method is suggested for the determination of free sulfur; it is based on reduction to hydrogen sulfide of the sulfate obtained by oxidizing the elemental sulfur which has been extracted with acetone.

The method has been checked on a standard solution of sulfur in acetone, on rocks containing free sulfur, and on Black Sea silt.

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SEPARATION OF SELENIUM AND TELLURIUM

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In its sexivalent state selenium is hardly coprecipitated at all with ferric hydroxide in an ammoniacal medium at a pH of 8 and higher. Quantitative separation of selenate ions from solution is only possible within the pH limits of the begining of complete precipitation of ferric hydroxide, i.e., up to a pH of 6 [1]. No published information could be found on the coprecipitation of sexivalent tellurium with ferric hydroxide, although it is known that quadrivalent tellurium can be separated quantitatively with lead hydroxide from solution. [2].

In the work described here we decided to establish how completely sexivalent tellurium can be separated with ferric hydroxide under conditions which are not favorable for coprecipitation of the selenate ion, and to study the possibility of separating selenium and tellurium.

Coprecipitation of tellurium with ferric hydroxide. Coprecipitation of tellurium was studied by means of its radioactive isotope–tellurium 127 [3]. For this purpose a solution containing the radioactive isotope of tellurium was prepared by dissolving metallic tellurium in nitric acid 1:1. The relative specific activity of this solution in terms of elemental tellurium corresponded to 123 000 impulses/minute/mg. In addition, a tellurium solution free from the radioactive isotope was prepared. The activity of the solutions was measured in glass cuvettes placed directly in a type AS-1 counter connected by a cable with a type B-2 radiometer. Usually, it did not exceed 1200-1500 impulses/minute. The pH of the solution was determined on a LP-5 potentiometer with a glass electrode.

First of all, several experiments were carried out on a study of the coprecipitation of tellurium oxidized to tellurous acid. The experiments were carried out as follows. Into a 250 ml conical flask was introduced a solution of ferric nitrate containing 15 mg Fe. To this solution was added a solution of tellurous acid in nitric acid, ammonium nitrate (coagulant), and water. The total volume of solution was about 50 ml, while the NH_4NO_3 concentration was 0.5 N. The amount of tellurium was varied. To a sample prepared in this way was added 4-5 ml of concentrated ammonia. The solution plus precipitate of ferric hydroxide were shaken by hand and then filtered.

The precipitate on the filter and on the flask walls was washed with an ammoniacal solution of ammonium nitrate. The filtrate and wash liquors were transferred into a standard flask from which an aliquot was taken for measuring the activity.

The pH of the solution was measured in the filtrate before washing the precipitate. The amount of coprecipitation (in %) was calculated from the amount of tellurium in solution. Both in this case and in subsequent experiments, control tests were carried out in which the activity of the dissolved precipitate was measured. As a rule, the total activity of the precipitate and filtrate plus wash liquors corresponded to the amount of activity introduced. The deviation did not exceed permissible experimental errors. Results of the experiments on coprecipitation of tellurium (IV) are given in Table 1.

In a similar fashion the coprecipitation of tellurium in the form of telluric acid with ferric hydroxide was studied. The telluric acid was prepared by oxidation of tellurous acid with excess 0.25 N potassium permanganate. Potassium permanganate was used as the oxidizing agent because it completely oxidizes both tellurous and selenous acid into telluric and selenic acids [4].

TABLE 1

Coprecipitation of Tellurium (IV) with Ferric Hydroxide

Tellurium taken, mg	pH	Tellurium coprecipitated	
		mg	%
0,025	9,50	0,025	100
0,050	9,60	0,049	98
0,100	9,52	0,100	100
0,250	9,59	0,250	100
0,500	9,45	0,500	100
1,000	9,49	1,000	100
1,500	9,65	1,488	99,2

TABLE 2

Coprecipitation of Tellurium (VI) with Ferric Hydroxide

Tellurium taken, mg	pH	Tellurium coprecipitated	
		mg	%
0,025	9,68	0,025	100
0,050	9,64	0,050	100
0,100	9,63	0,099	99,0
0,250	9,60	0,248	99,2
0,500	9,67	0 500	100
1,000	9,45	0,997	99,7
1,500	9,63	1,500	100

TABLE 3

Coprecipitation of Selenium (VI) with Ferric Hydroxide

Selenium taken, mg	pH	Selenium coprecipitated	
		mg	%
2,0	9,64	0,025	1,24
10,0	9,75	0,129	1,29
20,0	9,43	0,192	0,96
50,0	9,58	0,530	1,06
150,0	9,52	2,06	1,37

Results of the experiments on the coprecipitation of sexivalent tellurium are given in Table 2.

From Tables 1 and 2 it is evident that tellurite and tellurate ions can be isolated to the same extent fairly completely with ferric hydroxide from solution at a pH of 9.4-9.7.

Coprecipitation of sexivalent selenium with ferric hydroxide. Since coprecipitation of small amounts of selenous acid had been studied previously [1], on this occasion it was decided to study the coprecipitation of somewhat larger amounts of it.

The relative specific activity of the solution of selenous acid prepared corresponded, in terms of elemental selenium, to 3860 impulses/minute/mg. The relative error in measuring the activity did not exceed + 2%. Selenous acid not containing any of the radioactive isotope was used as an additive. The order in which the operations were carried out and the conditions used were the same as those used in the case of sexivalent tellurium.

It is clear from Table 3 that with increasing concentration of selenium in solution, the absolute amount of selenium (VI) coprecipitated also increases. However, the relative percentage coprecipitation does not change basically.

Coprecipitation of selenium and tellurium in each other's presence. In the first series of experiments, solutions of selenous and tellurous acid were mixed in definite proportions; one of the components of these mixtures contained a radioisotope. Subsequent operations were similar to those described above. In the second series of experiments, while the ratio of Se:Te and the other conditions were kept constant, the appropriate radioisotope of the other acid was used.

It is clear from Table 4 that at a pH of 9.5-9.7 sexivalent selenium is almost all found in solution, while the tellurium (VI) is quantitatively removed by the ferric hydroxide precipitate. Thus, it should be possible to separate tellurium and selenium. The present method can be used for concentrating small amounts of tellurium during the analysis of black selenium, and, possibly, for purifying selenium from tellurium. Where more complete separation is necessary, one could resort to a second precipitation, i.e., the Ferric Hydroxide is dissolved in nitric acid and the iron precipitated again in the presence of potassium permanganate.

The use of other metal hydroxides (instead of ferric hydroxide) for separating selenium and tellurium is not desirable, since selenium (VI) is coprecipitated to an appreciable extent with lead and bismuth hydroxides, while complete coprecipitation of tellurium cannot be effected with beryllium, aluminum, and titanium hydroxides.

TABLE 4

Coprecipitation of Se(VI) and Te(VI) in Each Other's Presence

Taken, mg		Ratio Te:Se	Te found in the precipitate		Se found in the precipitate	
Te	Se		%	mg	%	mg
15,0	5,0	3	99,8	14,97	1,46	0,07
10,0	5,0	2	99,8	9,98	1,04	0,05
5,0	5,0	1	99,7	4,99	1,22	0,06
2,5	5,0	0,5	99,6	2,49	0,52	0,03
0,1	5,0	0,02	100,0	0,10	0,94	0,05
0,1	10,0	0,01	99,9	0,099	0,62	0,06
0,1	25,0	0,004	100,0	0,10	1,72	0,43
0,1	50,0	0,002	99,9	0,099	1,20	0,60
0,1	100,0	0,001	100,0	0,10	1,14	1,14
0,02	200,0	0,0001	100,0	0,02	1,35	2,70

SUMMARY

A method suggested for separating selenium and tellurium is based on selective coprecipitation of tellurium (VI) with ferric hydroxide in a strongly ammoniacal solution. Selenium (VI) is hardly precipitated at all with ferric hydroxide under these conditions.

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CHEMICO-SPECTROGRAPHIC ANALYSIS OF HIGH PURITY ALUMINUM

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Modern industry produces aluminum with a purity of 99.998% [1-4] and even 99.9995% Al [5]. For controlling the production of material of such quality, use is made of the most sensitive methods of chemical analysis [6-14], radioactivation analysis [15-17], and, in particular, of spectrographic methods [6, 18, 19]. In order to increase the sensitivity of the spectrographic analysis of aluminum, various methods of concentrating the impurities are adopted. The physical enrichment method consists in evaporating the readily volatile impurities under vacuum and condensing them on the face of a copper or graphite electrode [20]. A number of methods have been described for the chemical concentration of impurities during analysis of high purity aluminum, e.g.: separation of traces of rare earths on a carrier – lanthanum [20]; successive precipitation of impurities with thioacetamide, ammonium pyrrolidinedithiocarbamate, and thionalide using thallium as collector [21]; extraction of impurities with organic solvents and with ammonium pyrrolidinedithiocarbamate and dithizone [22]. For this purpose the group reagents indicated should be of the highest purity.

The chemico-spectrographical method described below for the analysis of aluminum and its compounds consists in chemical concentration of the impurities, followed by their subsequent spectrographic determination.

The impurities are concentrated by removing aluminum by precipitating it in the form of the chloride $AlCl_3 \cdot 6H_2O$ with gaseous hydrogen chloride. During this process the impurities are concentrated in the mother liquor in which a little aluminum also stays. After reprecipitating the precipitate twice, the combined mother liquors are evaporated with nitric acid, the residue is calcined, and a concentrate of the impurities is obtained on a Al_2O_3 base. At the same time, a sample is prepared without enrichment; this is carried out by converting the sample into the nitrate, and then into aluminum oxide; this coincides with the final stage in the preparation of the concentrate. Standards are also prepared on an aluminum oxide basis. Control tests are carried out during the chemical preparation of samples and concentrated in order to take into account any contamination of the reagents used.

Spectrographic determination of the impurities is carried out on a ISP-22 spectrograph; the spectra being excited in a d.c. arc between carbon electrodes. 20 elements are determined simultaneously: Be, Mg, Ca, Ba, Ti, V, Mo, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Sn, Pb, Sb, Bi, In. The sensitivity of the method is 10^{-4}-10^{-6}% (Table 1). The increase in sensitivity following upon concentrating the impurities is shown in Fig. 1. The accuracy of the method is characterized by a relative error of ± 20% on an average.

Spectrographic analysis of samples without enrichment of the impurities can be used independently for controlling the production of less pure marks of aluminum.

Concentration of impurities. The method of separating aluminum from other elements by precipitating it as aluminum chloride hydrate on saturating a hydrochloric acid solution with gaseous hydrogen chloride is very selective, and has long been used both for preparing pure samples of aluminum chloride [23-26], and for the quantitative separation and determination of aluminum [25,27]. In the latter instance, various authors have precipitated aluminum chloride by saturating with hydrogen chloride hydrochloric acid solutions mixed with ether or acetone. Under such conditions it has been found possible to separate aluminum from Be, Ca, Mn, Fe, Co, Cu, Zn, Hg, and Bi [23-27]. A description has been given of the application of this technique for the chemical analysis of aluminum and its alloys for their content of certain impurities, e.g., beryllium [7,28].

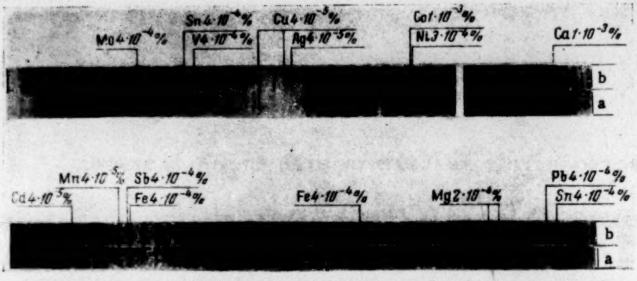

Fig. 1. Comparison of the spectrogram of aluminum (a) with a spectrogram of a concentrate of the impurities (b) for an enrichment coefficient k = 30 (the impurities were introduced artificially).

TABLE 1

Sensitivity of the Method and the Analytical Lines Used

Elements	Sensitivity obtained		Analytical lines, A	Elements	Sensitivity obtained:		Analytical lines, A
	without enrichment	enrichment coefficient k = 50			without enrichment	enrichment coefficient k = 50	
Be	$3\cdot10^{-4}$	$6\cdot10^{-6}$	2348,6	Cu	$1\cdot10^{-4}$	$5\cdot10^{-6}$	3247,5
Mg	$2\cdot10^{-4}$	$1\cdot10^{-5}$	2795,5	Ag	$1\cdot10^{-4}$	$2\cdot10^{-6}$	3280,7
Ca	$3\cdot10^{-3}$	$6\cdot10^{-5}$	4226,7	Zn	$1\cdot10^{-2}$	$2\cdot10^{-4}$	3345,0
Ba	$2\cdot10^{-2}$	$4\cdot10^{-4}$	4934,1	Cd	$3\cdot10^{-4}$	$6\cdot10^{-6}$	2288,0
Ti	$3\ 10^{-3}$	$6\cdot10^{-5}$	3234,5	Pb	$1\cdot10^{-3}$	$2\cdot10^{-5}$	2833,1
V	$2\cdot10^{-3}$	$4\cdot10^{-5}$	3185,4	Sn	$1\cdot10^{-3}$	$2\cdot10^{-5}$	2840,0
Mo	$1\cdot10^{-3}$	$2\cdot10^{-5}$	3132,6	Sb	$2\cdot10^{-3}$	$4\cdot10^{-5}$	2598,1
Mn	$1\cdot10^{-4}$	$5\cdot10^{-6}$	2794,8	Bi	$1\cdot10^{-3}$	$2\cdot10^{-5}$	3067,7
Fe	$2\cdot10^{-3}$	$4\cdot10^{-5}$	2720,9	In	$3\cdot10^{-4}$	$6\cdot10^{-6}$	3256,1
Co	$2\cdot10^{-3}$	$4\cdot10^{-5}$	3412,6	Cr	$1\cdot10^{-3}$		4254,3
Ni	$2\cdot10^{-3}$	$4\cdot10^{-5}$	3414,8				

Note. The values given for the sensitivity of the determination of Mg, Mn, Fe, and Cu take into account the possibility that these elements are present in the control experiment. Chromium was determined without enrichment.

In the chemico-spectrographic method of analyzing aluminum developed, there is no need to separate the aluminum quantitatively. After precipitation of most of the aluminum, the small amount of aluminum remaining in solution together with the impurities serves subsequently as a base for the powdered concentrate.

The solubility of aluminum chloride is strongly depressed on increasing the HCl concentration of the aqueous solution. Thus, in terms of 100 g of the saturated solution at 25° the solubility in water is 34.08 g $AlCl_3$, while for concentrations of 30.17 and 40.98 g of HCl respectively, the solubility is 2.49 and 0.98 g $AlCl_3$ [29]. The solubility of $AlCl_3 \cdot 6H_2O$ can be depressed further by cooling.

In our experiments, on precipitating $AlCl_3 \cdot 6H_2O$ with gaseous HCl while the solution was cooled with a mixture of ice and cooking salt, 0.5-0.7% of the aluminum remained in solution, while after a three fold precipitation (see below) the amount that remained was 1-5-2%; for an original aliquot of 5 g of aluminum this means that 75-100 mg of Al as metal or 150-200 mg as aluminum oxide remained in solution. This amount of oxide is quite enough for spectrographic analysis. When this technique was used, the enrichment coefficient (the ratio of the original aliquot of sample to the weight of the concentrate obtained, both in terms of aluminum metal) was 50-70 under the conditions developed.

The distribution of traces of impurities between the solid and liquid phases during precipitation of $AlCl_3 \cdot 6H_2O$ with gaseous hydrogen chloride was studied with synthetic mixtures. To solutions of spectrographically pure preparations of aluminum chloride (the method for purifying which is based on the same principle) was added known amounts of standard solutions of the impurity elements in amounts corresponding to 10^{-3}-10^{-5}% with respect to aluminum. The mixtures were analyzed by the method developed. Each phase was analyzed spectrographically: the combined fractions of mother liquor obtained after three successive precipitations, and also the aluminum chloride precipitate remaining after these precipitations.

The purity of this precipitate was controlled both by a direct spectrographic method, and also by repeating the operation of concentrating the impurities by additional reprecipitation of the precipitate. Table 2 contains as an example the results obtained during the analysis of two synthetic mixtures. Completeness of the concentration of the impurities during analysis of aluminum was controlled by the same method.

These experiments with synthetic mixtures and samples in which the various phases and fractions of mother liquor were controlled, showed that when the $AlCl_3 \cdot 6H_2O$ was precipitated three times with gaseous HCl, the following impurities, contained in the aluminum in trace amounts, are almost quantitatively concentrated in the mother liquor: Be, Mg, Ca, Ba, Ti, V, Mo, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Pb, Sn, Sb, Bi, In. Extraction of traces of the elements indicated into the concentrate (concentration 10^{-3}-10^{-5}) amounts to 85-100%.

Chromium is coprecipitated to a significant extent with the precipitate of $AlCl_3 \cdot 6H_2O$. The distribution of chromium between the phases was checked by means of the radioindicator Cr^{51}. In these experiments, on introducing $5 \cdot 10^{-3}$ and $5 \cdot 10^{-4}$% Cr^{51} into the aluminum chloride solution, and after precipitating the $AlCl_3 \cdot 6H_2O$, it was found that the hydrochloric acid mother liquor contained 4% and 15% respectively of the amount of chromium added. Coprecipitation of chromium was also confirmed by measuring the β-activity of the aluminum chloride precipitate. This behavior of chromium can presumably be attributed to isomorphous precipitation of $CrCl_3 \cdot 6H_2O$ with the precipitate of $AlCl_3 \cdot 6H_2O$, since the crystal structures of these salts are very similar [30].

TABLE 2

Analysis of Synthetic Mixtures (The amount of impurity element present is given as a percentage of metallic aluminum)

Elements	Mixture No.1 (coefficient k = 43.8)		Mixture No.2 (coefficient k = 48)	
	added	found	added	found
Be	$3\cdot10^{-5}$	$2,5\cdot10^{-5}$	$3\cdot10^{-4}$	$2,2\cdot10^{-4}$
Mg	$1,5\cdot10^{-4}$	$1,3\cdot10^{-4}$	$2,2\cdot10^{-3}$	$2,2\cdot10^{-3}$
Ca	$1\cdot10^{-3}$	$9\cdot10^{-4}$	$1\cdot10^{-3}$	$8\cdot10^{-4}$
Ba	$3\cdot10^{-4}$	$2,3\cdot10^{-4}$	$1\cdot10^{-3}$	$8,1\cdot10^{-4}$
Ti	$7,5\cdot10^{-4}$	$8\cdot10^{-4}$	$1\cdot10^{-3}$	$7,8\cdot10^{-4}$
V.	$1\cdot10^{-4}$	$1,1\cdot10^{-4}$	$5\cdot10^{-4}$	$3,3\cdot10^{-4}$
Mo	$3\cdot10^{-4}$	$3,1\cdot10^{-4}$	$5\cdot10^{-4}$	$6,2\cdot10^{-4}$
Mn	$1\cdot10^{-5}$	$1,3\cdot10^{-5}$	$2\cdot10^{-4}$	$1,7\cdot10^{-4}$
Fe	$3\cdot10^{-4}$	$3\cdot10^{-4}$	$3\cdot10^{-3}$	$2,7\cdot10^{-3}$
Co	$1\cdot10^{-4}$	$9\cdot10^{-5}$	$1\cdot10^{-3}$	$9\cdot10^{-4}$
Ni	$3\ 10^{-4}$	$3,9\cdot10^{-4}$	$4,2\cdot10^{-3}$	$3,1\cdot10^{-3}$
Cu	$4\cdot10^{-5}$	$3\cdot10^{-5}$	$1,5\cdot10^{-4}$	$1,2\cdot10^{-4}$
Ag	$4\cdot10^{-5}$	$4,2\cdot10^{-5}$	$4\cdot10^{-5}$	$5\cdot10^{-5}$
Zn	$3\cdot10^{-4}$	$2,2\cdot10^{-4}$	$3\cdot10^{-3}$	$2,7\cdot10^{-3}$
Cd	$4\cdot10^{-5}$	$3\cdot10^{-5}$	$3,6\cdot10^{-4}$	$2,3\cdot10^{-4}$
Pb	$1\cdot10^{-4}$	$1,10\cdot10^{-4}$	$1\cdot10^{-3}$	$1,2\cdot10^{-3}$
Sn	$3\cdot10^{-5}$	$2,4\cdot10^{-5}$	$3\cdot10^{-4}$	$3,8\cdot10^{-4}$
Sb	$3\cdot10^{-5}$	$2,3\cdot10^{-5}$	$8\cdot10^{-4}$	$1\cdot10^{-3}$
Bi	$3\cdot10^{-4}$	$4,3\cdot10^{-4}$	$5\cdot10^{-4}$	$5,6\cdot10^{-4}$
In	$1\cdot10^{-5}$	$1\cdot10^{-5}$	$1\cdot10^{-4}$	$1\cdot10^{-4}$

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k^* enrichment coefficient of the impurity.

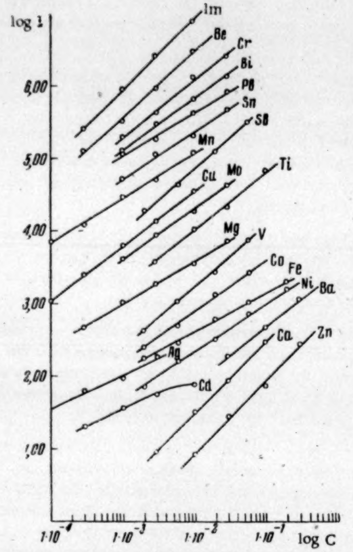

Fig. 2. Calibration curves for the determination of impurities in aluminum. The curves are arbitrarily shifted along the ordinate in order to avoid overlapping.

Using the radioindicator Ag^{110} it was confirmed that silver present as an impurity is concentrated: for a content of $2 \cdot 10^{-5}$ % of Ag in a synthetic mixture, after three successive precipitations, it was found that the mother liquor contained 84% of the Ag introduced.

Analytical Procedure

Preparation of the concentrate. 5 g of aluminum metal is placed in a 200 ml quartz flask and dissolved in 100 ml of 6 N HCl to which 0.2 ml of 14 N HNO_3 is added in order to dissolve and oxidize the impurities completely. Gaseous hydrogen chloride is passed through the cooled solution to complete saturation (40 minutes), the flask being cooled with ice or with a mixture of ice and cooking salt. After 20 minutes standing (in the cold) the solution is carefully poured off the precipitate. The precipitate of $AlCl_3 \cdot 6H_2O$ is dissolved in 70 ml of water after which it is reprecipitated with gaseous HCl. The precipitation is carried out a third time. All three mother liquors are combined and evaporated by gradually pouring them into a quartz beaker of about 50 ml capacity which has been heated beforehand at 550° and weighed. The residue of the salts obtained is converted into the nitrates by treating three times with small portions of 14 N HNO_3, the solution being evaporated each time to a syrupy state. The nitrates are calcined to the oxides at 550° and weighed. The enrichment coefficient of the impurities is then calculated: $K = M / 0.529 \cdot m$, where M is the weight of aluminum metal taken, in g; m is the weight of the concentrate obtained on the Al_2O_3 as a base, in g; 0.529 is the factor for converting Al_2O_3 to Al.

In parallel, a control test is carried out for each batch of reagents. For this purpose the same amount of water and acids as used for test samples is placed in a quartz flask, and gaseous HCl passed through the solution for the same time; a solution of spectrographically pure aluminum chloride (or nitrate) containing the equivalent of 100 mg Al is added; the solution is subsequently evaporated and the residue converted into the nitrate, which is then calcined and finally weighed. The conversion factor for the blank is calculated; this is equal to the ratio of the original aliquot of the aluminum sample (M) to the amount of aluminum introduced in the control experiment.

Preparation of sample without enrichment. Samples without enrichment are prepared either from an aliquot of the hydrochloric acid solution (the bulk of which is used for preparing the concentrate of the impurities), or from a separate aliquot. If the latter method is used 0.5 g of aluminum is dissolved in 6 N HCl, and the solution evaporated three times with 14 N HNO_3; the dry residue is calcined for 1 hour at 550° to give aluminum oxide.

Preparation of standards. Known amounts of standard solutions of the elements to be determined are added to a solution of spectrographically pure aluminum chloride. The solutions are evaporated to a syrupy state; by treating three times with 14 N HNO_3 the salts are converted into the nitrates which are then evaporated to dryness and converted to aluminum oxide. In this way a series of five standards are prepared, the composition of which is shown in the calibration curves (Fig. 2).

Standards and samples of aluminum oxide are stored in sealed weighing bottles, in a desiccator over phosphorus pentoxide.

Apparatus (quartz) flasks (200-300 ml), basins or beakers (50 ml), rods, tube for passing HCl into the solution. Reagents: water–twice distilled; hydrochloric and nitric acids –redistilled; gaseous hydrogen chloride.

prepared in a glass apparatus by heating concentrated HCl. The water and acids are distilled in a quartz apparatus, and are stored in quartz flasks.

Spectrographic analysis. Using the same conditions and with the same standards, the spectra of the concentrate of the impurities, and of the sample without enrichment, and the spectra of the material in the control experiment are photographed. The source is a d.c. arc with a current strength of 12 amp; the exposure is 2.5 minutes. Carbon electrodes are used (the lower electrode is a rod with a crater 4 mm in diameter and 6 mm deep on its end, while the upper electrode is sharpened to a point), they are fired for 15 seconds beforehand in the d.c. arc (12 amp) in order to free them from accidental contamination. 40 mg of powder is placed in the electrode crater and is moistened with 2 drops of a 20% alcoholic solution of bakelite; the mixture is then dried on a hot plate (the bakelite serves to prevent the sample from being thrown out of the electrode crater). The ISP-22 spectrograph is used, the slit width being 10μ. A two-stage attenuator with a relative transmission stage of 1:10 is set up in front of the slit. In the short-wave spectral region the lines are photographed in the weak stage, while in the long-wave region they are photographed in the strong stage of the spectrogram. Calibration curves (Fig. 2) are constructed within the coordinates log I, log c, where I is the line intensity (taking into account the background) and c is the concentration.

Conversion from blackening to intensity, with application of corrections for the background, is carried out by means of the characteristic curve on a special calculating apparatus. From the spectrograms of samples for which enrichment has not been carried out, the impurities present in high concentrations (10^{-1}-10^{-3}%) are calculated, while from the spectrograms for the concentrates, the impurities present in very small amounts and which have been concentrated are calculated (10^{-4}-10^{-5}%). In the latter instances the enrichment coefficient is taken into account when making the calculations.

Corrections for the amounts of impurities present in the reagents as found in the control test are applied to the analytical results, by using the conversion coefficients established.

SUMMARY

A chemico-spectrographic method has been developed for the analysis of high purity aluminum; it is based on chemical concentration of the impurities by separating the bulk of the aluminum by precipitation as $AlCl_3 \cdot 6H_2O$ with gaseous hydrogen chloride, and subsequent spectrographic determination of the impurities in the concentrate. 20 elements can be determined simultaneously: Be, Mg, Ca, Ba, Ti, V, Mo, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Pb, Sn, Sb, Bi, In. Thanks to an enrichment of the impurities of about 50 times, it is possible to increase the sensitivity of their determination to 10^{-4}-10^{-6}%. A technique has also been developed for the spectrographic analysis of samples in which the enrichment step is left out: this can be used for controlling technical production of aluminum in which the amount of impurities present is higher; the sensitivity of this technique is 10^{-2}-10^{-4}%.

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DETERMINATION OF SOME MICROIMPURITIES IN HIGH QUALITY SELENIUM

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For determining trace amounts of tellurium, copper, arsenic, gallium, antimony, and cadmium in high purity selenium we used neutron activation analysis. On bombarding with slow neutrons, as a result of nuclear reactions (n, γ) radioactive isotopes of the irradiated elements are obtained, the activity of which also serves as a measure of the amount of the elements to be determined. Since measurement of neutron flow is difficult and inaccurate, better results are given by a comparison of the activities obtained with the activities of known amounts of the elements to be determined, which have been irradiated under the same conditions. This method was also used in the work described here.

The principles and techniques of activation analysis have been described in a number of reviews and original papers [1-3]. A series of papers have been published on the determination of individual elements (Cu, Te, Ga, Sb, and As) in various materials [2,4-11].

Under the conditions we used, the theoretical sensitivity of the determination (for an induced activity towards the end of irradiation of 40 decays per second) amounts to (in g).

As (T 27 hours)	$3 \cdot 10^{-10}$ g
Cu (12.9 hours)	$5 \cdot 10^{-10}$ g
Ga (T 14 hours)	$5 \cdot 10^{-10}$ g
Sb (T 2.8 days)	$1.4 \cdot 10^{-8}$ g
Te (T 9.3 hours)	10^{-8} g
Cd (T 2.3 days)	$1.4 \cdot 10^{-8}$ g

Samples and standards were irradiated in a nuclear reactor under identical conditions. After addition to the sample of known amounts of inactive elements (carriers) in the form of various salts, the sample was dissolved and the elements to be determined subjected to chemical separation and purification. The activities of the separated elements were compared under identical counting conditions with the activities of standard samples, the chemical yields being taken into account.

Identical counting conditions were ensured by adopting the same form, dimensions, and amounts of materials in the samples and standards, and by using the same distance to the counter, etc. The precipitates to be used for activity determinations were filtered on dismountable glass filters.

The whole technique of separating and purifying the elements to be determined was developed using labeled atoms. It was shown that under these conditions the necessary radioactive purity was achieved. The latter was also controlled during the course of each analysis by determining the half-life period of the separated elements.

Separation and purification of test elements. After irradiation, the selenium sample (about 1 g) was washed with hot dilute HCl to remove any possible contamination on the surface. To the sample were added solutions of the salts of the carrier in amounts equivalent to 10-20 mg of the test element; the selenium was dissolved on heating in concentrated HNO_3, with subsequent careful evaporation of excess acid almost to dryness. The residue was dissolved in water and 1 g of urea added; the mixture was then boiled for about 10 minutes. To this solution was added HCl until the concentration of the latter was 6 N, this was followed by addition of 2.5 g of hydrazine sulfate. The solution was boiled under reflux for 5 minutes and the precipitate of elemental selenium filtered off. For more complete removal from the solution of radioactive selenium and gold activity, 20 mg of selenium in the form of selenous acid and 3 mg of gold (in the form of $HAuCl_4$) were added to the solution. A second boiling led to the separation of elemental selenium which was filtered off and rejected.

Isolation and purification of tellurium. After removing the selenium the filtrate was diluted with water until the HCl concentration was 2.7 N, about 1 g of Na_2SO_3 was added and the solution boiled for about 15 minutes. The precipitate of elemental tellurium was filtered off and washed with 2-3 N HCL, and then washed with water, and dissolved on heating in HNO_3 (1:3). The solution was filtered and evaporated to dryness. The dry residue was dissolved in 3% HCl and the solution boiled with urea. To this solution was added 20 mg of selenium (in the form of H_2SeO_3) and 3 mg of Au (in the form of $HAuCl_4$), copper (in the form of $CuCl_2$), and antimony (in the form of $SbCl_3$); this was followed by 10 mg of 10% KI solution, the whole was boiled and the precipitate of selenium and gold filtered off and rejected. To this filtrate hydrochloric acid was added until the normality was 2.7 N when the tellurium was precipitated with hydrazine. The precipitate of elemental tellurium was filtered through a tared filter with a blue band filter, and then washed with 2-3 N HCl, and with water; it was finally washed with alcohol and ether. The precipitate thus obtained was dried at 105° and weighed; the activity of the isolated preparation was determined on a torsion counter.

Isolation and purification of arsenic. After removal of tellurium, the filtrate was transferred to a distillation flask and $AsCl_3$ distilled off at 108-109°. To the distillate was added 10 mg of antimony (in the form of $SbCl_3$) and the distillation repeated. As_2S_3 was isolated by precipitating with H_2S, the precipitate was coagulated by boiling and was then filtered through a porous glass filter, it was washed first with concentrated HCl and then with water, and was dissolved on the filter in 25% ammonia. The solution was evaporated almost to dryness, 7 ml of concentrated HNO_3 was added and the solution again evaporated to dryness. The dry residue was dissolved in water, 100 mg of silver (as $AgNO_3$) was dissolved in water, 100 mg of silver (as $AgNO_3$) was added and silver arsenate precipitated with ten milliliters of a saturated solution of CH_3COONa. The precipitate was coagulated on a water bath and filtered off, it was then washed with hot water and dried; the activity was finally determined. The chemical yield was established by titrating the silver with a solution of NH_4SCN in the presence of ferric alum as indicator.

Separation of copper and antimony. After removal of the arsenic the solution was evaporated to 10 ml. To this solution was added 30 ml of water and 10 mg of silver (as $AgNO_3$). The AgCl was filtered off and rejected. To the solution was added 10 ml of a saturated solution of NaCl and cupric and antimony sulfides precipitated by means of Na_2S. The precipitate was filtered off; and washed with a solution which was 5% with respect to HCl and 10% with respect to NaCl it was then washed with water and transferred into a beaker.

Isolation and purification of copper. The precipitate of copper and antimony sulfides was treated with 10 ml of a mixture of 20% Na_2S and NaOH on heating on a water bath for about one hour. Copper sulfide was filtered off and washed first with dilute Na_2S solution and then with water, and finally dissolved in 3 N HNO_3 on heating. To this solution was added about 10 mg of iron as $Fe(NO_3)_3$ and 5% ammonia solution until there was a weak odor of the latter. The precipitate of $Fe(OH)_3$ formed was filtered off and rejected. The filtrate was acidified with sulfuric acid until the solution was weakly acid and copper rubeanate precipitated by means of $C_2H_4N_2S_2$, the rubeanate was filtered off and washed with dilute sulfuric acid, it was finally washed with dilute sulfuric acid and transferred to a beaker; to the latter was added 0.5 ml of concentrated H_2SO_4. The copper rubeanate was broken down by evaporating it with H_2SO_4. The solution was diluted with water to 50 ml; copper was reduced by passing sulfur dioxide through the heated solution for 15 minutes; $Cu_2(SCN)_2$ was formed by adding NH_4SCN, the former was filtered off through a tared blue band filter paper, it was washed with water saturated with sulfur dioxide, and then washed with alcohol and ether in turn, and dried at 105-115°; it was finally weighed and its activity measured.

Isolation and purification of antimony. To the solution was added 5 mg of copper as $CuCl_2$; CuS was filtered off and rejected. The filtrate was acidified with 2 N hydrochloric acid, the Sb_2S_3 formed was filtered off and washed with 2 N HCl, it was then treated with concentrated HNO_3 on heating. Trivalent antimony was oxidized with permanganate to the quinquevalent state and the latter extracted three times with diethyl ether. The ether was removed by heating, while the antimony was reduced with metallic iron to the elemental state in a hydrochloric acid solution to which was added 5 mg of tin as $SnCl_4$. The antimony precipitate was centrifuged and washed in turn with 3 N HCl and water and was then treated with concentrated nitric acid. The solution was evaporated. The precipitate of metaantimonic acid was suspended in 7 N HNO_3 and filtered through a blue ribbon filter paper, it was then dried and its activity measured. The precipitate was calcined in a porcelain crucible at 800° and then weighed.

Isolation and purification of cadmium. To the filtrate after removal of the sulfides of copper and antimony was added 5 mg of each of these elements in the form of their chlorides. The precipitate of the sulfides was then filtered off and rejected. NaOH was added until the solution was strongly alkaline; the CdS was filtered off and washed with a hot 5% Na_2SO_4 solution. The precipitate was transferred to a beaker to which was added about 5 mg of iron as $Fe_2(SO_4)_3$, and the mixture treated with 0.4 N H_2SO_4. The CdS was filtered off, washed, and then dissolved on the filter in 6 N HCl. The solution was boiled, about 10 mg of iron in the form of $Fe_2(SO_4)_3$ was added; followed by 5% ammonia solution until threre was a weak odor of the latter. The $Fe(OH)_3$ formed was filtered off and rejected. To the filtrate was added about 5 ml of a 10% solution of NaOH and cadmium sulfide precipitated with sodium sulfide. The CdS was filtered off, washed, and then reprecipitated from 0.4 N H_2SO_4. It was finally filtered through a blue band filter paper and its activity measured. The chemical yield of cadmium was determined by weighing it as $CdSO_4$; for this purpose the CdS was dissolved in the minimum amount of 6 N HCl, the solution was collected in a porcelain crucible,and concentrated H_2SO_4 added.The mixture was evaporated to dryness and then calcined at 500° and weighed.

Isolation and purification of gallium. After removal of cadmium the filtrate was neutralized with HCl, the Ga_2S_3 was filtered off and dissolved on the filter in 6 N HCl and was extracted twice with ether. The ether was removed by evaporation, to the solution left was added 10 mg of iron as $Fe(NO_3)_3$, and NaOH then added until its concentration in the solution was 0.5 N. The $Fe(OH)_3$ formed was filtered off and rejected. $Ga(OH)_3$ was deposited from the filtrate on neutralizing, the gallium hydroxide was washed with hot water, and dissolved on the filter in dilute HNO_3. $Ga(OH)_3$ was then reprecipitated by means of NH_4OH. The precipitate was filtered off through a blue band filter paper, it was washed and dried, and its activity measured. In order to determine the yield of gallium the precipitate was calcined at 1300° and weighed.

Purification of the standards. Standards, two for each test element, were prepared by placing 0.1 ml of the appropriate solution in a quartz target and drying off the solution. The target was placed in a quartz weighing bottle. The standards were subjected to two-three chemical purifications using a carrier for the test sample and using suitable back carriers.

The self-screening effect in the samples was taken into account; this is connected with a decrease (as a result of absorption by the materials of the sample) in the neutron stream from the periphery of the sample to the center. Under the experimental conditions used this effect was of the order of 3%.

In the course of this work the possibility of the formation of arsenic from selenium as a result of reactions with rapid neutrons (n,p) and with γ-rays (γ,p) was checked. It was established that as a result of such reactions, from one gamma of selenium there are formed radioactive isotopes of arsenic, whose activity was equivalent to the activity from $2 \cdot 10^{-8}$ g of arsenic.

Using the technique developed we have analyzed a number of samples of pure selenium. Below are given the results for one of the samples. (in percentages):

$$\text{Te}—1{,}2\cdot10^{-4}\ \ \text{Ga} < 10^{-7},\ \ \text{Cd}—4{,}5\cdot10^{-6}$$

$$\text{As}—1{,}9\cdot10^{-5},\ \ \text{Cu}—6\cdot10^{-6},\ \ \text{Sb}—1{,}6\cdot10^{-5}$$

SUMMARY

A technique has been developed for the determination of trace amounts of tellurium, copper, gallium,

arsenic, antimony, and cadmium in selenium by radioactivation analysis. The method suggested for the chemical separation and purification of the test elements makes it possible to isolate preparations of radiochemical purity. The chemical yield of carriers for copper, arsenic, and cadmium amounts to 50-70%, while for tellurium it is 30-50%, and for antimony and gallium 25-35%. The accuracy for the determination of individual elements is 10-25%.

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BOXES OF NEW DESIGN FOR WORK WITH RADIOACTIVE MATERIALS

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Analytical and preparative work with radioactive materials requires complete insulation of workers, not only from the main mass of the materials being treated, but also from the smallest splashes of solutions or from dust particles. Most analytical preparative or research work consists of a number of successive operations which demand different apparatus, and the latter, as a rule, cannot all be housed in one hermetically sealed box. Shifting of test material from box to box, and also storing of radioactive materials should be carried out in containers which are completely insulated from the surrounding space.

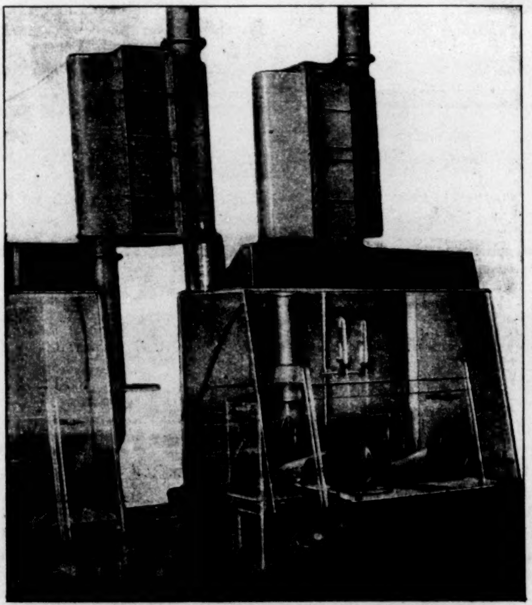

Fig.1. Working box. Aerosol filters are fitted on the walls.

For this purpose we have developed a set of boxes; these include a working box, a centrifuge box, and a balance box. They are all connected up to each other through any distance by means of a standard system of locks fitted into the boxes and portable cassettes.

The American glove boxes [1] known to the authors are not universal in the sense that they can be used for all operations. Samples must be introduced either through an open door in the side wall of the box, or through some box locks such a method of introduction, and, particularly, extraction of radioactive preparations gives rise to the danger of contamination of the air and laboratory equipment by radioactive splashes and dust.

The working, centrifuge, and balance boxes are shown in Figs. 1, 2, and 3 respectively. They are made from plexiglass 10 mm thick. The bottoms of the boxes are made of a vinyl plastic and are fused to the walls. The walls are glued together by means of dichloroethane.

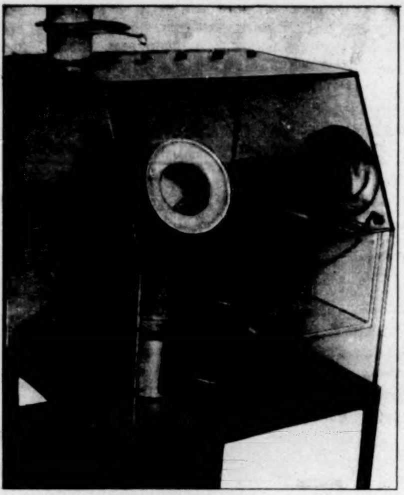

Fig. 2. Centrifuge box.

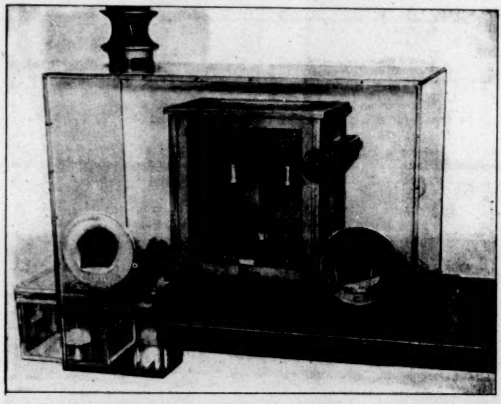

Fig. 3. Balance box.The handles for operating the ADV-200 balance are brought out through the front wall of the box.

The working box (Fig. 1). has the following basic outer dimensions: width 1000 mm, depth 620 mm, and height 700 mm. The front wall, with openings for the gloves, slopes, and can be taken down for assembling large apparatus. There are inlets for vacuum, compressed air, and electric terminals on both walls of the box.

The dimensions of the centrifuge box (Fig.2) are as follows: width 640 mm, depth 600 mm, and height 680 mm. The box is designed for a TsE-3 centrifuge of the medicinal type. It is also used for washing precipitates.

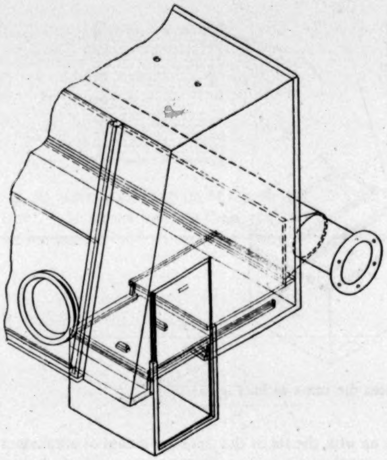

Fig. 4. Appearance of part of the working box. The outer cover of the lock is opened for introducing the cassette.

The balance box (Fig.3) is used for balances of the type ADV-200 and MV-20 and has the following dimensions: width 900 mm, depth 450 mm, and height 600 mm. The handles of the balance are brought outside.

All the boxes have outlets for connecting to a system of extractive ventilation through aerosol filters. Locks (Fig. 4 and 5) are welded into the bottoms of the boxes (working and balance) or in the side wall (centrifuge box). Both the boxes, as well as the cassettes and locks can also be prepared from other materials (various plastics, stainless steel, etc).

Lead glass or a sheet of lead metal can be fitted onto the outside of the forward wall and also inside the box for protection against γ-radiation.

The casette of the working box fits the lock of any of the boxes. The casette (Figs. 5 and 6) is used for transferring radioactive preparations from one box into another, for introducing reagents and small apparatus into the boxes, for storing radioactive materials, and also for removing various waste products. It is a sealed box 13 with a lid 10 having protrusions 2, and can be moved along corresponding grooves in the walls of the box. The configuration of the grooves in the box and the protrusions in the lid ensure close sealing of the casette. The grooves on the outer perimeter of the casette serve as guides for placing the box in a lock (during this operation they link up with the protrusions 3 on the lock), and also for fixing the casette in a definite position inside the lock. At the same time, the protrusion 3 and the part of the casette above the protrusion act as seals during opening of the lid of the casette and the lock.

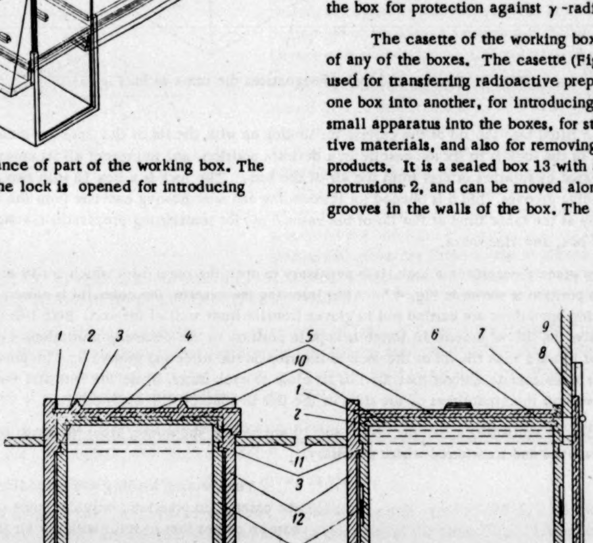

Fig. 5. Front view (from the left on the plan) and side view (on the right) of the box fitted into a lock. 1) Protrusion on the casette lid; 3) protrusion (groove) on the lock wall (of the casette); 4) controlling protrusions of the lock lid; 5) lock lid; 6) outer lid of the lock; 7) controlling groove; 8) groove of the outer lid; 9) side wall of the box; 10) casette lid; 11) box bottom; 12) lock; 13) cassette.

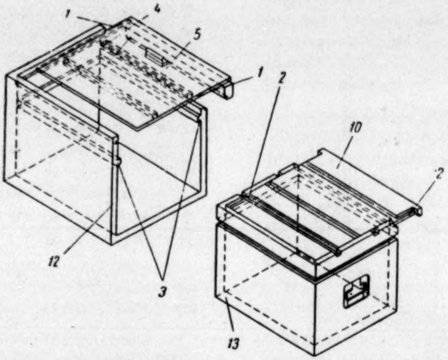

Fig. 6. Casette and lock (designations the same as for Fig. 5).

Groves are fitted into the lid of the casette for linking up with the lid of the lock by means of protrusions 4. The purpose of the lock is to fix the casette in a definite position, and to protect all its outer surfaces from being contaminated by splashes or dust from the air of the box. The lock is a box 12 with two lids which slide along corresponding grooves. Lid 6 is opened for introducing and withdrawing casettes from the lock, while lid 5 is opened (only at the same time as the lid of the casette 10) for transferring preparations, reagents, etc; from a casette into a box, and vice versa.

In order to place a casette in a lock, it is necessary to open the outer lid 6 which is slid along the directing grooves 8. This position is shown in Fig. 4 *. After inserting the casette, the outer lid is closed (Fig. 5) and all the remaining working operations are carried out in gloves from the front wall of the box. Both lids can only be opened simultaneously: the lid of casette 10 which is kept in position by the directing protrusions 4 on the lid of lock 5, is shifted forward with the lid of the lock to the stop on the directing groove 7. The position of groove 3 on the perimeter of the casette ensures that the lids fit close to each other, while the fact that they are opened simultaneously ensures the cleanliness of the sides of the lids in contact with each other.

After loading or unloading a casette, lids 5 and 10 are closed, the worker frees his hands from the gloves and the casette is removed and transferred where necessary.

Thus, during loading and unloading operations with the casette, in practice, only the inner surface of the casette comes into contact with the air in the box, while all the outer surface of the casette and the inner surface of the lock are protected from contamination; this guarantees the cleanliness of the casette on the outside, and consequently makes it possible using such a casette to transfer radioactive materials from one box to the other and also into storage.

A gap of about 2 mm is left between the lock and the casette below the groove on the perimeter of the casette; this gap prevents air being sucked out of the box on withdrawing the casette from the lock, and facilitates its withdrawal. All the grooves are lubricated for free shifting of the casette in the lock.

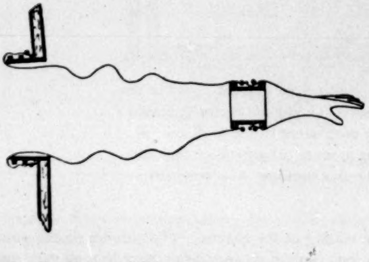

Fig. 7. Fixing of the gloves in a box.

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* All the details are not given in Figs. 4, 5, and 6.

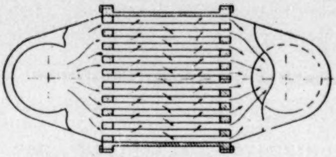

Fig. 8. Schematic diagram of the aerosol filter. The arrows indicate the direction of air movement.

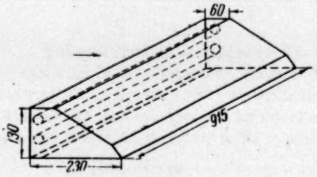

Fig. 9. Illuminator.

The construction of the casette permits the lock in the box to be shifted both to the right and the left of the worker. The construction of the casette also permits the same casette to be placed in both the right and left lock. Casettes and locks are made from 10 mm thick plexiglass. The grooves are milled, while the protrusions and seals are glued on. The main outer dimensions of the casette are: height 200 mm, width 200 mm, depth 250 mm.

For working with such boxes, with the air being constantly sucked out, normal medical gloves fastened to long sleeves made of rubber about 1 mm thick are used; the sleeves are fitted onto the flanges of the openings in the forward wall of the box.

The medical gloves wear out very rapidly, while the sleeves are seldom removed from the box. Moreover, repeated use of the sleeve for gluing is difficult because its surface gets contaminated with radioactivity.

The sleeve and glove are connected together by means of a device in the form of a wristband. The wristband is a plastic cylinder oval in form. Its dimensions are such as to ensure that the wrist can be passed through it in order to put on the gloves. The length of the wristband is 60-70 mm. At its outer edges the wristband has two flanges which ensure close connection of the wristband with the sleeve on the one hand and with the glove on the other. The sleeve and glove are fitted to the wristband by means of rubber bands (Fig. 7). As established in practice, such a setup permits easy replacement of the gloves, and also facilitates working without limiting the mobility of the wrist.

Each box is connected via an aerosol filter to an exhaust fan. 6-8 boxes are connected to two parallel exhaust fans(type EVR-2). This ensures that the exhaust fans can be used continually. The vacuum thereby created inside the box (a few mm of water) causes an intensive draft of air from the laboratory through fine slits, so that there is no need for rubber packing, screw lids, etc.

The intensity of the draft and the throughput capacity of the filters is calculated so as to ensure an air flow of not less than 2.0 meters/second in one glove hole when it is disconnected or a glove is changed.

A schematic diagram of the aerosol filter is shown in Fig. 8.

The filter element is a band of acid-resistant, folded filter cloth (mark FPP-1) 1.5 cm^2 in area, between the layers of which are inserted wooden frames in the form of the letter П. A bundle of such frames with the filter cloth is stretched on each side with bolts, and to the bundle, from two sides are connected air storage tanks of light sheet iron painted with acid-resistant paint, or tanks made from vinyl plastic. The filter is hung on the wall behind a box. The general appearance of the filter and its position on the wall is shown in Fig. 1. The filter can readily be replaced. The connecting air tubes between box and filter and the common air pipe are vinyl plastic tubes (d = 105 mm) which are connected to each other and to the boxes and filters by means of flanges with rubber packing, or are welded together. A valve is fitted between a box and its filter for regulating the vacuum in the box and for switching of the latter from the common system.

The illuminator used in the box, consisting of two luminescent tubes type DS-30 with reflectors, allows the light beam to be concentrated only on the working surface of the box, and also protects the eye of the worker from direct light (Fig. 9).

SUMMARY

Glove boxes of new design are suggested which permit radioactive materials, chemical glassware, and

small apparatus to be transferred from one box to another without exposing the worker's hands to radioactive contamination, and which prevent contamination of the laboratory air.

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A SPOT METHOD FOR DETECTING THIOETHER AND THIOKETONE SULFUR IN MEDICINAL PREPARATIONS AND IN SOME BIOLOGICAL MATERIALS

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Thioether and thioketone sulfur can be detected in organic compounds by reduction to the sulfide ion or by oxidation to the sulfate ion. These methods, however, do not permit detection of bound sulfur in a test material, and, moreover, they are difficult to carry out. The iodoazide reaction [1-5] first studied by Raschig, [6] is widely used as a spot test for thioether and thioketone sulfur in organic and inorganic compounds. This reaction is used for detecting sulfur in protein materials [1,2,7] and for organic medicinal materials [8].

Some sulfur-containing organic compounds on simple heating, or on heating in the presence of such weak reducing agents as glucose or starch, liberated hydrogen sulfide [9] which can be detected by means of sodium nitroprusside. Some other organic compounds which we studied also liberated hydrogen sulfide on heating (ammonium thiocyanate, essential oil of mustard, thiourea,cysteine,cystine, thibone, thyphene, norsulfazol,penicillin, methylthiouracil).

We have established that on fusing thioethers and thioketones with a crystal of sodium hydroxide in a test tube, sodium sulfide is readily formed which gives with a 1% solution of sodium nitroprusside a stable intensely red or red-violet color. On this basis we have developed a simple spot method for detecting thioether and thioketone sulfur in organic medicinal preparations, plant materials, sulfur-containing essential oils, amino acids,and some protein materials.

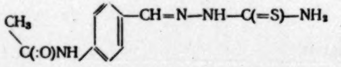
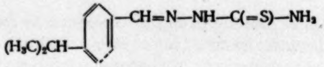
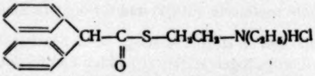
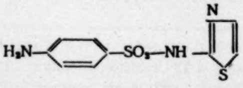
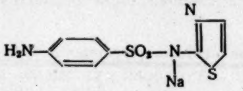
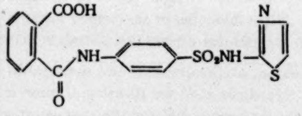
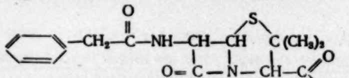
Detection of thioether and thioketone sulfur in medicinal preparations. 1 drop of a 2-3% solution of the test material in 10% sodium hydroxide, or a mixture of about 0.005 g of material and 1 drop of 10% sodium hydroxide, are evaporated to dryness in a porcelain microcrucible on an electric hotplate covered with an asbestos mat, and the residue carefully heated until a reddish or light-brown color appears; on cooling, 1-2 drops of 0.1% aqueous sodium nitroprusside is added. When thioether or thioketone sulfur is present an intense red or red-violet color develops. The sensitivity of the reaction for various compounds is given in the Table.

For establishing the sensitivity of detection, a 1% solution of test material in a 10% solution of sodium hydroxide is successively diluted with water five times until the limiting dilution is attained. The optimum ratio of the concentration of the solution of the test compound and the concentration of the sodium hydroxide solution is 1:10.

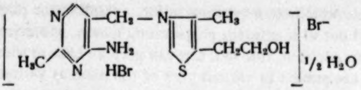
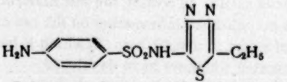
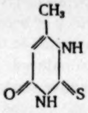
In order to detect sulfur in cutizon and thyphene which are insoluble in alkali solutions, alcoholic solutions of cutizon and aqueous solutions of thyphene are used; these are mixed in a microcrucible in the proportions indicated with sodium hydroxide solution and are then tested as described above.

Ichthiol and albichthol, which are mixtures of sulfonated thyphenes and also phenothiazine derivatives (phenothiazine and methylene blue) do not give the color reaction. Negative results were also obtained on testing a number of organic medicinal preparations containing sexivalent and quadrivalent sulfur (sergosine, analgine, sulfodiamine and sulfanilamide preparations which do not contain the thiazol or thiodiazol groups).

Sensitivity of Sulfur Detection

Preparation	Chemical formula and rational designation	Limiting dilution	Limit of detection, γ
Ammonium thiocyanate	$NH_4—N=C=S$	1 : 10 000	2
Essential oil of mustard	$CH_2=CH—CH_2—N=C=S$ Allyl isothiocyanate	1 : 10 000	1
Thiourea	$H_2N—C\ (=S)—NH_2$	1 : 20 000	1
Cysteine	$H_2C\ (SH)\ CH\ (NH_2) — COOH$ α-Amino-β-thiopropionic acid	1 : 40 000	0,5
Cystine	$HOOC—CH\ (NH_2) — CH_2—S—S—CH_2—CH\ (NH_2)— —COOH$ Di-α-amino-thiopropionic acid	1 : 20 000	1,5
Thibon	 p-Acetaminobenzaldehyde thiosemicarbazone	1 : 10 000	3
Kutizone	 p-Isopropylbenzaldehyde thiosemicarbazone	1 : 20 000	2
Thyphene	 The hydrochloride of the β-diethylaminoethyl ether of thiodiphenylacetic acid	1 : 4000	5,2
Norsulfazol	 2-(p-Aminobenzenesulfamido)-thiazol	1 : 5000	6
Soluble norsulfazol	 Sodium salt of norsulfazol	1 : 3300	6
Phthalazol	 2-(p-Phthalaminobenzenesulfamido)-thiazol	1 : 4000	5
Penicillin	 Potassium salt of benzenepenicillin	1 : 4000	5

Continuation of Table

Preparation	Chemical formula and rational designation	Limiting dilution	Limit of detection, γ
Vitamin B_1 (thiamin bromide)	 The hydrobromide of N-(2-methyl-4-amino-5-methylpyrimidine)-methyl-5-β-hydroxyethyl-thiazolium bromide	1 : 8000	2,5
Ethazol	 2-(p-Aminobenzenesulfamido)-5-ethyl-3,4 thiodiazol	1 : 5000	4
Methyl-thiouracil	 6-Methylthiouracil	1 : 4000	5

The reaction suggested permits identification of the test medicinal preparations and allows them to be distinguished from other sulfur-containing organic compounds; in particular, it permits sulfanilamide preparations containing thiazol and thiodiazol groups to be distinguished from other sulfanilamides. We have also used the reaction described for differentiating penicillin from other antibiotics. Under the conditions used, gramicidin C, levomycetin, syntomycin, streptomycin, and biomycin gave negative results. It must be emphasized that the reaction described, in contrast to the Lassaigne test, can be used for differentiating a number of other derivatives of the classes of sulfur-containing compounds listed above. Tests have also shown that it is possible to use the reaction suggested as a spot test for detecting thiosulfate ions which contain divalent sulfur.

The presence of sulfide ions interferes with detection of sulfur. However, in contrast to the iodoazide reaction, the presence of sulfide ions in a test solution can readily be established by a preliminary spot test with sodium nitroprusside [1].

Detection of thioether and thioketone sulfur in plant materials and protein materials. We have used the spot reaction described for studying certain plant materials containing biologically active materials whose molecules contain thioether and thioketone sulfur. We took some heads of onions (Allium cera) and garlic (Allium sativum) which are rich in essential oils, the main component of which are the disulfide $C_6H_{12}S_2$; seeds of Brassica juncea and Brassica nigra, containing the glucoside sinigrin; seeds of Sinapis alba containing the glucoside sinalbin; roots of Raphanus sativus and Armorica rusticana which contain an appreciable percentage of the antibiotic lizomycin [10], which in its chemical composition is a polypeptide with five cystine residues [11]. Sulfur was found in all the materials indicated. For examining onions and garlic, a slice of 1-2 mm^3; was placed in a microcrucible and 2 drops of a 1% sodium hydroxide solution added the mixture was evaporated the appearance of a light-yellow color (the mixture is not heated to dryness); it was then cooled and 1-2 drops of a 0.1% sodium nitroprusside solution added. The appearance of a red-violet or red color which was stable for 1-1.5 minutes indicated the presence of a sulfur-containing essential oil. The method of detecting lizomycin in Raphanus sativus and Armorica rusticana differed only in the use of a 2% sodium hydroxide solution. For detecting sulfur-containing glucosides in the seeds of various types of mustard, one seed was crushed in a microcrucible by means of a glass rod, a drop of 2% sodium hydroxide solution was added and the procedure outlined above for onions and garlic followed. A red-violet color which was stable for about one minute was obtained. The presence of appreciable amounts (up to 35%) of fatty oil in the mustard seeds did not interfere. Similar results were obtained with mustard powder.

Thus, the reaction suggested permits one to establish the presence of various sulfur-containing organic materials with strong biological action in test plant materials. This reaction may be used as a diagnostic sign for ascertaining the nature of unknown plants (thus the presence of the sulfur-containing glucosides sinigrin and sinalbin is characteristic of the Cruciferae alone). Using this reaction it is possible to distinghish between essential oils which contain sulfur and those which are free from sulfur, both in the plant itself, and also on the pure materials. Experiments carried out with aniseed, peppermint, lemon, and thyme oils which do not contain sulfur gave negative results. In addition, this spot test can give an idea of whether sulfur containing essential oils, glucosides, or antibiotics are present in various parts of the plant at various periods in the growth of the plant.

For the detection of sulfur in sulfur-containing amino acids and proteins during biochemical studies, the reaction usually adopted is formation of lead sulfide on boiling the test material in a mixture of lead acetate and sodium hydroxide solutions. There is no published information on the use of this reaction for carrying out spot tests. A spot reaction for detection of sulfur in natural horn [2] which is based on formation of iron thiocyanate is more complicated than the reaction which we have developed.

We have succeeded in getting positive resultsduring detection of sulfur in one drop of egg albumen and in salive. Particularly good results are given by materials containing keratin: wool fiber, hair, and horn tissue. About 5 mm of fiber, 5-6 cm of hair, or about 0.003 g of horn tissue was mixed with two drops of 10% sodium hydroxide in a microcrucible, the mixture was evaporated to dryness, it was then cooled and 1-2 drops of 0.1% sodium nitroprusside added to the residue. When keratin was present an intense red-violet color appeared. Silk fiber which does not contain sulfur gave a negative result under these conditions. Cotton did not give a positive result either. On this basis we have used the method of detecting keratin described for distinguishing wool from silk and cotton. The color of wool fabric did not interfere with the reaction. This method can also be used to establish whether horn being tested is genuine.

The advantages of the spot reaction described for biochemical studies are its simplicity, the ease with which it can be carried out, and the insignificant amount of test material required.

The author wishes to thank V. N. Bernshtein for directing the work described here.

SUMMARY

A spot method which is described for detecting thioether and thioketone sulfur in certain medicinal preparations, plant materials, sulfur-containing essential oils, amino acids, and proteins is based on formation of sulfide on sintering the test material with sodium hydroxide. Sodium nitroprusside is used as the reagent.

The sensitivity of the reaction for ammonium thiocyanate, essential oil of mustard, thiourea, cysteine, cystine, thibon, cutizon, thyphene, norsulfazol, soluble norsulfazol, phthalazol, penicillin, thiamine, and methylthiouracil varies from 0.5 to 6γ.

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DETERMINATION OF THE STRUCTURE OF PARAFFIN AND NAPHTHENIC HYDROCARBONS BY INFRARED SPECTROSCOPY

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In the present article, which is devoted to a description of further work on the structure of the hydrocarbons of the kerosene fraction of motor fuel [1-2], a method is suggested for the determination of the number of CH_2- and CH_3-groups in strongly branched paraffins and 6-membered naphthenic hydrocarbons, which is based on their infrared spectra in the region 2800-3000 cm^{-1}. Since chemical methods of studying the structure of such complex compounds are difficult, while these compounds are finding greater use in modern techniques, the problem of their structure is a pressing one.

The problem of determining the number of CH_2- and CH_3-groups in hydrocarbons has attracted the attention of research workers before [3-9], but the methods suggested have either only been applied to slightly branched hydrocarbons or have involved very complicated experimental procedures.

Rose [3] has shown that the groups CH_3, CH_2, CH, and $CH_{aromatic}$ have several characteristic peaks in the interval 5000-9000 cm^{-1}, and measurement of the intensity of such peaks permits determination of the number of these groups in a molecule, as long as their mutual overlapping is taken into account. However, the formulas which he suggested, in view of changes in the extent of overlapping of the bands, have not always proved reliable. In a particular, for branched hydrocarbons, the error in determining the number of groups may be as much as 30-50%. Moreover, a considerable amount of test material (10-15 ml) is required for analysis in the overtone region because of the very weak absorption.

An almost identical study was carried out by Hastings [4] for the region of valence CH-vibrations (2800-3000 cm^{-1}). The calculating formulas he derived also give satisfactory results for normal paraffins and low molecular weight naphthenes, but these formulas can lead to significant errors when determining CH_3- and CH_2-groups in high molecular weight compounds (C_{12} and higher).

Interesting results for normal paraffins were obtained by Jones [9]. By careful measurement of the peak intensity of the bands at 2930 and 2965 cm^{-1}, which relate to vibrations of CH_2 and CH_3 groups respectively, he established that there is a strict proportionality between the number of CH_2-groups and the intensity of the 2930 cm^{-1} peak. On an average, the molar absorption coefficient (ϵ) for one CH_2-group amounted to 74 units. No direct relation was established for the 2965 cm^{-1} peak. This deviation from proportionality in the changes of ϵ for the 2965 cm^{-1} band (as the results of this work and [4] show) is explained by overlapping of the 2930 and 2965 cm^{-1} bands.

Egorov and Petrov [1] have suggested a graphical method for determining the number of CH_3- and CH_2-groups in C_{12}-C_{16} paraffins, which is based on measuring the ratio of the absorption of the 2930 cm^{-1} peak to that of the 296 cm^{-1} peak. This method permits one to determine comparatively accurately and rapidly the average degree of branching of hydrocarbon fractions which do not contain very complex paraffins; the method is, however, not applicable to highly branched molecules.

It might be mentioned that analysis of paraffins in the region 2800-3000 cm^{-1} has the advantage that it only requires a very small amount of material (about 30 mg). In addition, the 2930 and 2965 cm^{-1} bands in the infrared spectra of this class of compounds are characteristic and hardly change their position at all in molecules of different structure.

Some authors [5-7] have studied the region of deformation frequencies in CH_3 (1360-1470 cm^{-1}) and CH_2-groups (720, 1300, and 1460 cm^{-1}). It has been established, however, that the peak intensities of the bands are not proportional to the number of methyl and methylene groups; in addition, in a number of instances, the frequencies in the spectra of branched paraffins split up. The use of these methods is not so convenient, since it becomes necessary to determine the integral intensities of the bands examined, and this is very difficult in practice.

Taking into account the advantages and disadvantages of the methods which have been briefly described, and also bearing in mind our own work in this field [1,2,10], we concluded that measurement of the peak intensities of the two absorption bands of valence CH-vibrations at 2965 and 2930 cm^{-1}, taking into account mutual overlapping in each individual case, makes it possible to determine the number of CH_2- and CH_3-groups satisfactorily in branched paraffins. We also established that the number of these groups in naphthenes of the type C_6H_{11}-R, where R is aliphatic, can be established by measurement of the intensities of the same bands. The latter proved to be possible because the absorption bands of the CH_2-groups of a six-membered ring do not differ in position, and, as it turned out subsequently, do not differ in intensity either, from the bands of CH_2-groups in paraffins.

TABLE 1

Intensities of the Absorption Bands at 2930 and 2965 cm^{-1} in Paraffins

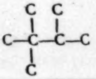
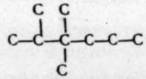
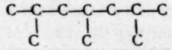
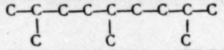
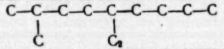
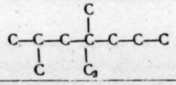
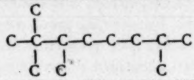
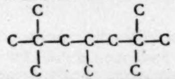
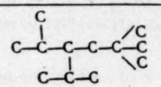
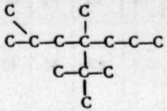
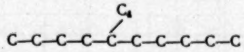
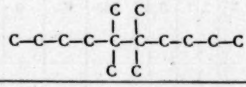
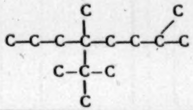
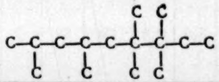
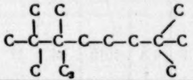
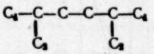
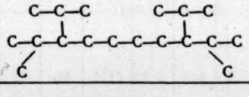
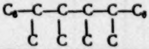
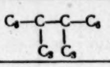
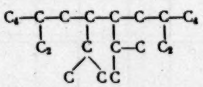
		ε_{2965}	P_1	n_1	n_1'	Δn_1	ε_{2930}	P_2	n_2	n_2'	Δn_2
C_7H_{16}		440	88	5	4,5	0,5	—	—	—	—	—
C_8H_{18}		420	84	5	4,3	0,7	105	105	1	1,2	0,2
$C_{10}H_{22}$		550	110	5	5,6	0,4	170	85	2	2,0	0,0
$C_{12}H_{26}$		480	96	5	4,9	0,1	350	88	4	4,0	0,0
$C_{12}H_{26}$		370	93	4	3,8	0,2	520	87	6	6,0	0,0
$C_{12}H_{26}$		640	128	5	6,5	1,5	460	92	5	5,3	0,3
$C_{12}H_{26}$		590	98	6	6,0	0,0	250	83	3	2,9	0,1
$C_{12}H_{26}$		650	93	7	6,7	0,3	170	85	2	2,0	0,0
$C_{12}H_{26}$		600	86	7	6,2	0,8	120	120	1	1,4	0,4

TABLE 1 (Cont'd)

		ε_{2960}	P_1	n_1	n'_1	Δn_1	ε_{2930}	P_2	n_2	n'_2	Δn_2
$CH_{13}H_{28}$		690	98	7	7,1	0,1	230	77	3	2,6	0,4
$C_{14}H_{30}$		340	113	3	3,5	0,5	830	83	10	9,5	0,5
$C_{14}H_{30}$		570	95	6	5,9	0,1	530	88	6	6,1	0,1
$C_{14}H_{30}$		670	96	7	6,9	0,1	340	85	4	3,9	0,1
$C_{15}H_{32}$		680	85	8	7,0	1,0	260	87	3	3,0	0,0
$C_{15}H_{32}$		770	110	7	7,9	0,9	410	82	5	4,7	0,3
$C_{16}H_{34}$		390	97	4	4,0	0,0	860	86	10	9,9	0,1
$C_{18}H_{38}$		800	100	8	8,2	0,2	350	88	4	4,0	0,0
$C_{20}H_{42}$		600	100	6	6,2	0,2	860	86	10	9,9	0,1
$C_{20}H_{42}$		380	95	4	3,9	0,1	1200	85	14	13,8	0,2
$C_{24}H_{50}$		720	90	8	7,4	0,6	810	81	10	9,3	0,7

$P_{1_{\text{mean}}} = 97$ $\Delta_{1_{\text{mean}}} = 0,4$ $P_{2_{\text{mean}}} = 88$ $\Delta_{2_{\text{mean}}} = 0,2$

TABLE 2

Intensities of the Absorption Bands at 2930 and 2965 cm^{-1} in Six-Membered Naphthenes

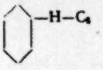
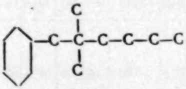
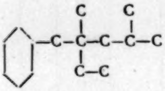
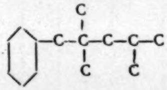
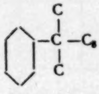
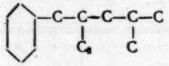
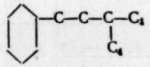
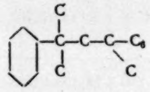
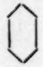
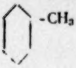
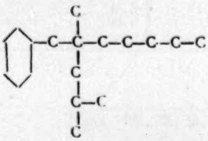
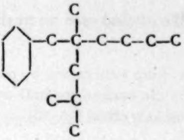
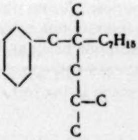
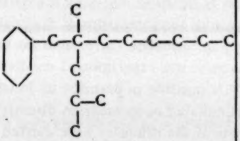
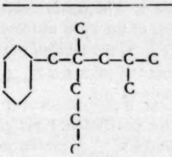
	Σ_{2930}	P_1	n_1	n'_1	Δn_1	Σ_{2965}	P_2	n_2	n'_2	Δn_2
	160	160	1	1,6	0,6	860	86	10	9,7	0,3
	270	90	3	2,7	0,3	740	82	9	8,4	0,6
	380	95	4	3,8	0,2	750	94	8	8,5	0,5
	360	90	4	3,6	0,4	580	83	7	6,6	0,4
	290	96	3	2,9	0,1	1010	84	12	11,5	0,5
	300	100	3	3,0	0,0	1100	92	12	12,5	0,5
	230	115	2	2,3	0,3	1170	90	13	13,3	0,3
	380	95	4	3,8	0,2	940	86	11	10,7	0,3
	—	—	—	—	—	535	89	6	6,1	0,1

TABLE 2 (Cont'd)

	Σ[illegible]	P_1	n_1	n'_1	Δn_1	Σ[illegible]	P_2	n_2	n'_2	Δn_2
	120	120	1	1,2	0,2	450	90	5	5,1	0,1
	430	107	4	4,3	0,3	990	90	11	11,3	0,3
	420	105	4	4,2	0,2	870	87	10	9,9	0,1
	400	100	4	4,0	0,0	1170	90	13	13,3	0,3
	390	98	4	3,9	0,1	1100	92	12	12,5	0,5
	400	100	4	4,0	0,0	820	91	9	9,3	0,3

$P_{1_{\text{mean}}} = 99 \quad \Delta n_{1_{\text{mean}}} = 0,2; \quad P_{2_{\text{mean}}} = 88 \quad \Delta n_{2_{\text{mean}}} = 0,35$

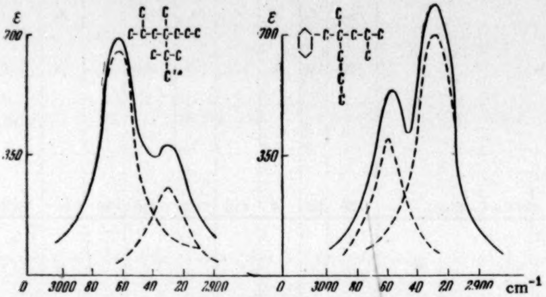


Fig. 1.

The experimental procedure adopted is described below, together with the method used for treating the spectral results obtained.

The compounds which we tested and which are listed in Tables 1 and 2 were synthesized by published methods [11, 14]. The structural formulas given can be regarded as correct on the basis of spectral and chemical results. In some doubtful cases we carried out additional studies by the usual method [15-17].

Infrared absorption spectra were obtained for each paraffin and naphthene in the region 2800-3000 cm^{-1} on an IKS-11 spectrometer fitted with a LiF prism. The thickness of the absorbing layer was 0.1 mm while the width of the inlet and outlet slits of the apparatus was 0.13 mm. In order to obtain reliable results the spectrum of each compound was recorded 4-5 times. Our main attention was given to the absorption bands at 2930 and 2965 cm^{-1}, which relate, as pointed out already, to antisymmetric vibrations of CH_2- and CH_3-groups respectively [1]. In Fig. 1 are given as examples the absorption curves for a paraffin and a naphthene in the part of the spectrum we were interested in.

As an analysis of the contours of the bands considered showed, their shape can be regarded as symmetrical and is fairly accurately described by a dispersion formula. On this basis the complex total contour can be resolved into its individual components. An example of such a resolution is shown in Fig. 1 by the dotted line. In almost all cases this leads to good results for subsequent determination of the intensities of the peaks. In order to get the true value of the optical density (D_0) it is normally necessary to introduce corrections for the final slit width of the apparatus [10]. A consideration of this question as it relates to our experimental conditions showed that for a slit width of 0.13 mm (6 cm^{-1} according to the spectrum) it is possible in practice to do without the correction, since it did not increase D_0 by more than 1.05 times. This enabled us to measure directly the observed value of the peaks obtained after resolution. Further calculations of the intensity were carried out by means of the usual formula: $\epsilon = D_0 / cd$, where $\underline{c}$ is the concentration in g.mole/liter, and $\underline{d}$ is the layer thickness in cm. The final experimental results are summarized in Tables 1 and 2. The tables include: the formula of the test compound; the values of ϵ found experimentally on the basis of the 2930 and 2965 cm^{-1} bands; the number of units of intensity per CH_2- or CH_3-group ($p = \epsilon / n$) (where $\underline{n}$ is the number of the appropriate groups); the true number of groups $\underline{n}$; the number of groups actually found n' ($n' = \epsilon / P_{mean}$ and the difference between the true and experimentally determined number of groups $\Delta n = [n - n']$.

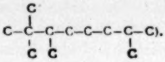
The results given in Tables 1 and 2 confirm that the value of the extinction coefficient P per group (CH_2 or CH_3) is independent of the structure of the hydrocarbon chain. For CH_2-groups P_{mean} proved to be 100 units, while for CH_2-groups it was found to be 90 units. As is evident, the deviation of the number of CH_3- and CH_2-groups found from the true value($\Delta n = [n - n']$ is not great and does not exceed 0.5 of a group; this means, in many cases, that it is possible to decipher the structure of individual compounds, and also to get an idea of the average degree of branching of mixtures (Table 3).

TABLE 3

Determination of the Mean Degree of Branching of Mixtures

Composition of the mixture, %		Mean number of CH_3-groups		Error, %	Mean number of CH_2-groups		Error, %
normal	branched	calc.	found		calc.	found	
79,0	21,0	2,84	2,97	4,6	8,53	8,00	6,2
53,5	46,5	3,86	3,60	6,8	6,75	7,20	6,6
48,5	51,5	4,06	4,20	3,50	6,40	6,63	3,6
39,0	61,0	4,10	4,00	2,5	5,73	6,15	7,3
28,0	72,0	4,88	4,70	3,7	4,96	4,90	1,3
		Mean		4,2	Mean		5,0

(Mixtures are made up of two components each of which are C_{12} hydrocarbons: 1) a normal paraffin and 2)



$$\mathrm{C-\overset{C}{\underset{C}{C}}-\underset{C}{C}-C-C-C-\underset{C}{C}-C}).$$

The significant deviations from the mean values of P_1 and P_2 observed in some cases (e.g., Table 1) may be explained by inaccuracies in resolving the bands or by insufficient purity of the test compound.

On can expect that by using a better apparatus, a two-lens spectrometer with a fairly good resolving power, the efficiency of the method could be considerably increased and the possible applications of the method extended.

SUMMARY

A method is suggested for determining the number of CH_2- and CH_3-groups in highly branched paraffins and in six membered naphthenes.

The mean extinction coefficients of certain infrared absorption bands which relate to valence vibrations of CH_2- and CH_3-groups have been determined, and it has been shown that they are additive in character.

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THE QUANTITATIVE DETERMINATION OF HALOGEN IN ORGANIC COMPOUNDS

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The rate of interaction between chlorine-containing organic compounds and potassium iodide (RCl + KI → RI + KCl) in anhydrous acetone has been studied in connection with the mobility of chlorine [1]. The reaction rate has been measured on the basis of the amount of potassium iodide entering into the reaction, excess of the iodide being titrated with 0.003 M sodium iodate in a hydrochloric acid medium in the presence of chloroform [2]. In one paper [3] the reaction with potassium iodide has been used for the quantitative determination of 1-chloro-3-methylbutane in the presence of 1-chloro-2-methylbutane. K. V. Lets et al [4] have determined certain primary chlorides by their reaction with an urotropine complex (KI + urotropine + acetone); the amount of mobile chlorine was determined from the amount of urotropine used.

We were interested in the possibility of using the reaction with KI for the quantitative determination of the mobile chlorine of organic compounds in the presence of halogen derivatives whose chlorine has low mobility.

The reaction was carried out with a saturated solution of potassium iodide in anhydrous acetone, while the amount of potassium iodide which had reacted was determined from the amount of potassium chloride which settled out of solution. We could not make use of the titration of potassium iodide with sodium iodate in a hydrochloric acid medium, since, in the case of unsaturated halogen derivatives, as our experiments showed, the method does not always give good results.

Potassium chloride is almost insoluble in anhydrous acetone, while potassium iodide is readily soluble and can be completely separated from potassium chloride. The potassium chloride is washed free from traces of potassium iodide, it is then dissolved in the minimum possible amount of water and is finally titrated by the Mohr method. The organic halogen derivative is removed during the washing process.

The organic halogen derivatives used had the chlorine on the primary carbon atom; they included: benzyl chloride, cuminyl chloride, cuminylidene chloride, β-phenylallyl chloride, allyl chloride, methylallyl chloride, isobutyl chloride, 2-methyl-4-chlorobutene-2 (isoprene chloride), monochloroacetic acid, etc.

In the case of benzyl chloride, the reaction takes a more than three days to go to completion at room temperature; at 50° the reaction is 98% complete after 3 hours, while at the boiling point of acetone the reaction is 99-100% complete. From the results given in Table 1 it is clear that all the compounds we tested, which had the chlorine on the primary carbon atom and an active group in the α-position (double carbon-carbon bond, benzene ring, carboxyl group) react quantitatively with potassium iodide in anhydrous acetone, although the reaction rate differs for the various chlorides. The compound which reacts most readily with potassium iodide is monochloroacetic acid; in the case of allyl chloride and methylallyl chloride on the other hand, the reaction only goes to completion after boiling for four hours.*

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* It should be noted that the reaction with potassium iodide in anhydrous acetone is the only method for determining these two compounds, without counting the method of elemental analysis, of course.

TABLE 1

Halogen derivative	Duration of the reaction hours	Weight of sample taken	Chloride found,%
Benzyl chloride	2	0,0897	84,7
" "	3	0,1073	99,9
Cuminyl chloride	2	0,0897	87,9
" " "	3	0,1040	100,0
Phenylallyl chloride, primary	2	0,1333	95,1
" "	3	0,1020	99,0
Allyl chloride	3	0,0949	89,3
" "	4	0,0989	98,3
Methylallyl chloride	3	0,0983	92,7
" "	4	0,0907	99,7
Monochloroacetic acid	1	0,0826	94,6
" "	2	0,0803	95,6
2-Methyl-4-chlorobutene-2-	1	0,0890	85,0
"	2	0,1047	98,7
Geranyl chloride	0,5	0,1129	73,6
" "	1	0,1032	75,6

TABLE 2

Mixture	Taken,%	Found,%	Mixture	Taken,%	Found,%
Benzyl chloride and benzylidene chloride	66.8	66.2	Cuminyl chloride and cuminylide chloride	31.57	31.53
" "	12.67	12.64	" "	15.40	15,43

Benzylidene chloride and cuminylidene chloride do not react with potassium iodide, while the corresponding monochlorides are quantitatively converted into the iodides. This fact means that it should be possible to develop a method for the separate determination of mono- and dichlorides in each others presence. We should point out that the method used for benzyl chloride, in which it is saponified with 0.5 N alcoholic potassium hydroxide, is not suitable for its separate determination since the dichlorides also partially react (10-15%) under these conditions.

Separate determination of benzyl chloride and cuminyl chloride in the presence of benzylidene- and cuminylidene chloride was carried out on synthetic mixtures. Total chlorine was determined by saponification with 0.5 N alkali in 50% aqueous ethylene glycol; in order to enhance the solubility of benzyl chloride, a mixture of 25% ethanol and 25% water was used instead of the 50% water.

The geranyl chloride used for our work was prepared by Pigulevskii's method [6], and had the following constants: $n^{20}D$ 1.4771; d^{20}_4 0.9274 (published data [6]: $d^{19}D$ 1.4796; d^{20}_4 0.9295). The following chloride values were found for this material; 98% by saponification with alcoholic alkali, 75% by the reaction with KI in anhydrous acetone, and 74.7% by the reaction with the urotropine complex. A comparison of these results leads one to suggest that the sample we used actually contains about 75% of the primary chloride (geranyl chloride) and 25% of chlorides which are not determined by this method. This fact was confirmed by infrared spectroscopy and by combination scattering spectra. The combination scattering spectrum had the following intense lines (in cm^{-1}): 672, 925, 990, 1162, 1225, 1252, 1324, 1379, 1431, 1662 and 1673. The presence of the two frequencies C=C 1662 and 1673 cm^{-1} is in agreement with the structure of geranyl chloride in which there are two non-terminal C=C bonds. A band with a frequence of 920 cm^{-1} was observed in the infrared spectrum; this indicates the presence of small amounts of terpenyl chloride.

Both terpenyl chloride and isobutyl chloride which have the chlorine atom on the tertiary carbon atom do not react with potassium iodide. Accordingly, the sample which we tested actually only contains about 75% geranyl chloride, and the reaction with potassium iodide correctly characterizes its purity.

EXPERIMENTAL PROCEDURE

The acetone used was dried over calcium chloride and then distilled; it contained $\leq$ 0,3% of water; the latter was determined by the Karl Fischer method.

The potassium chloride was dried for one hour at 120° before it was dissolved in the acetone; the solution was stored over $CaCl_2$ in a desiccator.

An aliquot of the halogen-containing test material (about 0.1 g) was placed in a 100-150 ml flask together with 30 ml of the saturated solution of potassium chloride. The reaction mixture was boiled under reflux on an air bath until potassium chloride had finished separating out (0.5, 2, 4, etc., hrs).

When the reaction was complete, 10 ml of anhydrous acetone was added to the flask through the condenser, and after 10-15 minutes heating the reaction mixture was passed through a glass filter. The precipitate was washed with anhydrous acetone until the washings gave a negative test for iodide (test with $AgNO_3$ solution). The precipitate which had been washed with acetone was dissolved in a small volume of water and the chloride ion determined in the aqueous solution by the Mohr method.

Total benzyl and benzylidene chlorides were determined by a method published previously [5]; the only difference in the method was the use of 0.5 N alkali in aqueous-alcoholic ethylene glycol (50% ethylene glycol-25% water-25% ethanol) to enhance the solubility of benzyl chloride.

Benzylidene chloride, cuminylidene chloride, tertiary isobutylchloride, and terpenyl chloride do not react with KI.

Results for the determination of benzyl chloride and cuminyl chloride in their mixtures with the corresponding dichlorides are given in Table 2.

SUMMARY

A method has been developed for the quantitative determination of certain primary chlorides by the reaction with potassium iodide in anhydrous acetone.

It has been established that benzylidene chloride, cuminylidene chloride, isobutyl chloride (tertiary), and terpenyl chloride do not react with potassium iodide.

A method is suggested for the separate determination of benzyl chloride and cuminyl chloride in their mixtures with the corresponding dichlorides; a method is also suggested for the determination of geranyl chloride in the presence of linalyl- and terpenyl chlorides.

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PHYSICOCHEMICAL METHODS OF DETERMINING ANTIBIOTICS

COMMUNICATION 9. A PHOTOMETRIC METHOD FOR THE DETERMINATION OF POLYMYXIN *

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In order to control the fermentation process of producing polymyxin, and also for controlling the characteristics of the finished product, a reliable method for its quantitative determination is required. The biological method is not suitable because it takes a long time and the results obtained are not accurate enough. Chemical methods of determining polymyxin B by means of the ninhydrin reaction [1,2] and phosphotungstic acid [3] are complicated and are not suitable for production conditions.

In order to determine the polymyxin content of a solution we used the biuret reaction which is widely used for the quantitative determination of proteins of plant and animal origin [4]. Polymyxin, which is polypeptide in nature, also gives with a cupric sulfate solution in the presence of caustic alkali a violet color which is characteristic for a biuret complex.

Ion exchange resins are used at present in polymyxin production during the process of its chemical purification. The ion exchange resins are used for separating polymyxin from compounds of a protein nature which are formed at the same time as polymyxin during biosynthesis. The eluates obtained on desorbing polymyxin from the ion exchange resins with a solution of acid in methanol, as well as the concentrates and dry preparations of polymyxin, hardly contain any impurities which give the biuret reaction. This means that it is possible to use the biuret reaction for the quantitative determination of polymyxin in the preparations mentioned.

After carrying out experiments at various concentrations of the reagent solutions, we decided to use a 0.5% cupric sulfate solution and 0.5 N caustic alkali.

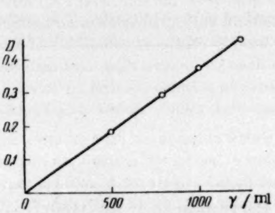

Fig. 1. The relation between the optical density D and polymyxin concentration.

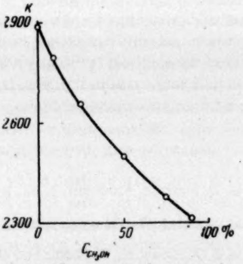

Fig. 2. The relation between the proportionality coefficient K and methanol concentration.

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* For Communication 8 see "Med.Ind. USSR," No.4, 49 (1959).

Determination of the polymyxin content of a solution by means of the biuret reaction consists of the following: to 10 ml of a polymyxin solution with a concentration of 500-1500 γ/ml is added 10 ml of 0.5% cupric sulfate and 4 ml of 0.5 N caustic alkali. The precipitate of cupric hydroxide which is formed is filtered off and the optical density of the transparent filtrate which has a violet color is measured (a cuvette with a layer thickness of 5 cm). The polymyxin concentration of the solution is determined by means of a calibration curve. The color which develops as result of the reaction between polymyxin and copper is fairly stable and remains constant for 1 hour. The optical density is directly proportional to the polymyxin concentration of the solution (Fig. 1).

Glycocol, histamine, and sodium chloride have hardly any effect on the optical density of the solution; methanol increases it. This fact should be borne in mind when determining the polymyxin content of methanol solutions. The polymyxin concentration of solutions containing methanol is calculated by means of the formula $C = D \cdot K$, where C is the polymyxin concentration of a solution in γ/ml, D is the optical density, and K is the proportionality coefficient.

The relation between the values of the proportionality coefficient and the methanol content of the solution is shown in Fig. 2. Knowing the methanol content of a test solution, the corresponding value of K is found.

Test material	Polymyxin found:	
	chemically	biologically*
Dry preparation	1030	1000
	1000	960
	940	920
	800	830
	880	900
Concentrates, eluates (in γ/ml)	45500	45100
	13100	13150
	37500	39200
	4600	4570
	21600	20600

*Mean of 12 determinations

The method described for determining polymyxin is fully reproducible; it takes 10-15 minutes to carry out. It permits determination of polymyxin in dry preparations and also in concentrates and eluates obtained on desorbing polymyxin (from ion exchange resins by means of acid methanol). The results are in good agreement with the results of a direct biological determination of the activity of these preparations by the method of diffusion in agar (Table).

Impurities which are always present in culture liquids interfere with the determination of polymyxin in these liquids. For separating polymyxin from culture liquids it is possible to use its basic properties which ensure that it is readily adsorbed by cation exchange resins. Preliminary work along these lines has shown that polymyxin can be quantitatively sorbed from culture liquids by means of the ion exchange resin KB-1, and can be completely eluted from the resin by a solution of hydrochloric acid in methanol. The eluate obtained is free from the impurities which interfere with polymyxin determination. From the polymyxin content of the eluate it is possible to calculate thre polymyxin content of the original culture liquid.

We should like to thank V. S. Dmitrieva and N. A. Bol'shakova for their assistance.

SUMMARY

A method is suggested for the quantitative determination of polymyxin which is based on a reaction between polymyxin and divalent copper in the presence of alkali, during which a violet color develops. The optical density of the solutions is directly proportional to the concentration of the antibiotic. The method permits determination of polymyxin in dry preparations as well as in the concentrates and eluates obtained on desorbing polymyxin from cation exchange resins.

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BRIEF COMMUNICATIONS

A NEW REACTION FOR DIVALENT COPPER IONS

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The reaction suggested is based on the formation of a brown-red precipitate during the interaction of Cu^{2+} ions with p-toluidine (p-$CH_3C_6H_4NH_2$) and hydrogen peroxide. The reaction is carried out by adding sodium acetate to the solution which is to be tested for copper ions until the pH is 6-7; this is followed by 1 ml of a saturated solution of p-toluidine and 2 drops of 3% H_2O_2 solution. When cupric ions are present a brown-red precipitate is formed. The precipitate is soluble in organic solvents and in acids to give a cherry colored solution. The color is stable. When the reaction is carried out in a test tube the sensitivity is 0.3γ ml; when it is carried out on a porcelain plate it is 0.038 γ ; the limiting dilution is 1:4,000,000.

Other cations, apart from Fe^{2+} ions which give a similar reaction, do not interfere with detection of copper; interference from Fe^{2+} can be overcome by oxidizing it to Fe^{3+} with nitric acid. The presence of cations which are readily hydrolyzed depresses the sensitivity somewhat. In such cases, when the copper content is low, the reaction should be carried out by a spot technique. For this purpose, a drop of test solution plus precipitate, 1 drop of a saturated aqueous solution of p-toluidine, and 1 drop of 3% hydrogen peroxide are placed successively on a filter paper. When copper is present the edge of the spot is colored an intense cherry.

This reaction has been used for the "non-destructive" determination of copper in aluminum alloys.

EXPERIMENTAL TECHNIQUE

On the surfaces of the test alloy and of an alloy with a known content of copper, small "baths" of the same size are made of paraffin or wax,. It is also possible to place a layer of paraffin 3-5 mm thick on the surface of the alloy, and then in the middle of the surface covered with wax make a small crater. In this crater, which has been cleaned from oxides beforehand, is placed 1 drop of HCl (1:1) and 2 drops of concentrated HNO_3. During the dissolution process the mixture is stirred with a glass rod. After 3-5 minutes the solution is transferred by means of a capillary to a porcelain crucible. The surface of the samples is washed with water and the wash liquors combined with the main solution. One drop each of HCl and HNO_3 are added to the contents of the crucible and the whole heated on a water bath; the solution is finally evaporated to dryness. A few drops of water are added to the residue in the cooled crucible, and the residue from each test transferred to equal measuring cylinders. The crucibles are rinsed out with water. To each cylinder are added 10 drops of a saturated solution of sodium acetate, 4 drops of a saturated aqueous solution of p-toluidine, and 2 drops of 3% hydrogen peroxide. After 5 minutes 10 drops of H_2SO_4 (1:1) is added. Under these conditions a color which is stable with time is formed.

To the cylinder with the solution whose color is most intense is added distilled water until the color of the solutions in both cylinders is the same. A note is made of the volumes of the solutions in the cylinders. Knowing the copper content of the standard sample, the copper content of the test alloy is calculated by means of the formula: $C_1 = V_1/V_2 \cdot C_2$, where C_1 is the copper content of the test alloys, C_2 is the copper content of the standard sample, and V_1 and V_2 are the corresponding volumes.

A determination takes 15-20 minutes. The results obtained agree with the results obtained by an iodometric method and by an electrogravimetric method.

SUMMARY

A new, selective, and highly sensitive reaction is suggested for cupric ions; it is based on the formation of of a colored reaction product when cupric ions interact with p-toluidine and hydrogen peroxide. The reaction has been used for the "non-destructive" determination of copper in aluminum alloys.

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DETERMINATION OF COBALT BY RADIOMETRIC TITRATION WITH POTASSIUM FERROCYANIDE

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I. V. Tananaev and M. I. Levina [1] having studied in detail the system $CoSO_4 - K_4[Fe(CN)_6] - H_2O$ by a physicochemical method, concluded that the reaction between $CoSO_4$ and $K_4[Fe(CN)_6]$ proceeds in three stages: formation of two double salts and solid solutions of variable composition. Subsequently [2], the same authors studied the same system by means of the isotope Ag^{110} in order to establish the relative stability of the metal bonds in the outer sphere of the mixed ferrocyanides with the ferrocyanide ions.

In our opinion, of considerable interest is the radiometric titration of cobalt ions with a solution of $K_4Fe(CN)_6$ using Co^{60} as indicator.

The $CoSO_4$ solution contained 0.62 mg of $CoSO_4$ in 1 ml.

The normality of 0.004 M $K_4[Fe(CN)_6]$ was established by titrating it with a solution of potassium permanganate using methyl violet as indicator ($T_{K_4[Fe(CN)_6]} = 1.47$ mg/ml).

A $CoSO_4$ solution containing the radioactive isotope Co^{60} was prepared by dissolving metallic cobalt containing Co^{60} in sulfuric acid. Excess acid was removed by evaporation. The cobalt sulfate obtained was dissolved in distilled water and the solution diluted appropriately to lower its specific activity. The solution thus prepared contained 0.8139 mg $CoSO_4$ per ml.

Checking the composition of the cobalt ferrocyanide precipitate. Into graduated centrifuge tubes were introduced 2 ml each of the inactive and 1 ml each of the active $CoSO_4$ solutions. To each of these tubes was then added various volumes of $K_4[Fe(CN)_6]$ solution (from 0.2 to 1.3 ml) and the total volume in each tube made up to 5 ml with distilled water.

After 20 minutes in a water bath at 60-70°, the tubes and their contents were centrifuged for 20 minutes. By means of a special apparatus and a pipet, 1 ml of each centrifuge was transferred from the tubes to a 2 ml crucible.

The activity of the samples of centrifugate taken was measured on a type B setup.

In Table 1 and Fig. 1 are given the results for a radiometric titration of $CoSO_4$ with $K_4[Fe(CN)_6]$ solution. The designation "control" is applied to the activity of 1 ml of the mixture (2 ml of inactive and 1 ml of active $CoSO_4$ solution) which has been diluted with distilled water to 5 ml and to which no $K_4[Fe(CN)_6]$ solution has been added.

In the initial stages of the titration the experimental results lie quite well on a straight line. Subsequent deviation of the titration curve from linearity can be explained by the appreciable solubility of the cobalt ferrocyanide precipitate.

Further addition of $K_4[Fe(CN)_6]$ solution is not expedient in the given instance, since, according to Langer's results [3], during radiometric titration in which soluble precipitates are formed, the equivalence point is determined by extrapolating the linear section of the titration curve to null activity, and construction of the whole titration curve is not necessary [4,5]. Thus, the linear section of the curve which we obtained during radiometric titration of $CoSO_4$ with $K_4[Fe(CN)_6]$ solution is more than sufficient for graphical determination of the volume of $K_4[Fe(CN)_6]$ solution required for binding the Co^{2+} ions completely.

TABLE 1

Determination of the Composition of the Cobalt Ferrocyanide Precipitate by Radiometric Titration

Crucible No.	$K_4[Fe(CN)_6]$ solution added, ml	Activity of 1.0 ml of mother liquor after subtracting background, imp/min	Crucible No	$K_4[Fe(CN)_6]$ solution added, ml	Activity of 1.0 ml of mother liquor after subtracting background, imp/min
Control	0	2002	7	0,8	1267
1	0,2	1789	8	0,9	1085
2	0,3	1692	9	1,0	983
3	0,4	1494	10	1,1	1012
4	0,5	1482	11	1,2	906
5	0,6	1394	12	1,3	868
6	0,7	1289			

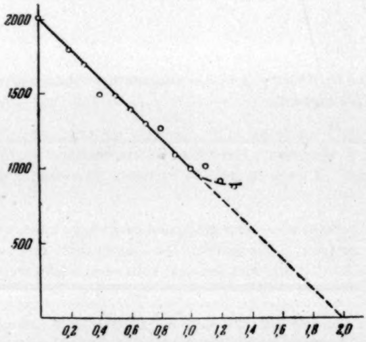

Fig. 1. Determination of the composition of cobalt ferrocyanide precipitate by means of the radiometric titration curve.

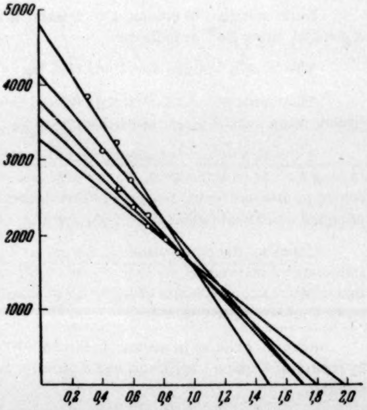

Fig.2. Radiometric titration curves of cobalt with potassium ferrocyanide.

When the acidity of the solution was high it was observed that the precipitate dissolved appreciably. In such cases it was necessary to add small amounts of sodium acetate or ammonia until the pH was 5.0-5.5. Within this pH range no shift in the equivalence point was observed.

Radiometric titration establablished that at low concentrations of $CoSO_4$ and $K_4[Fe(CN)_6]$, the composition of the precipitate can be expressed by the formula $5Co_2[Fe(CN)_6] \cdot K_4[Fe(CN)_6]$ or (what is the same) – $K_4Co_{10}[Fe(CN)_6]_6$; this formula is in complete agreement with that established by Tananaev and Levina by a physicochemical analytical method.

Radiometric determination of small amounts of cobalt. Results of radiometric titration are given in Table 2 and in Fig. 2.

TABLE 2

Determination of Cobalt by Radiometric Titration

Co taken, mg	Amount of standard $K_4[Fe(CN)_6]$ solution added V_1 ml	Activity of 1 ml of mother liquor after subtracting background imp/min		Amount of titrated solution at the equivalence point V_x, ml	Co found, mg	Error, %
		A_0	A_1			
0,7808	0,7	3271	2139	2,016	0,7910	+1,30
0,7808	0,9		1793	1,989	0,7804	—0,06
0,7337	0,6	3543	2390	1,842	0,7227	—1,50
0,7337	0,8		1933	1,760	0,6887	—6,14
0,6866	0,5	3791	2617	1,61	0,6317	—8,0
0,6866	0,7		2275	1,75	0,6866	—
0,6394	0,4	4116	3112	1,63	0,6396	+0,04
0,6394	0,6		2749	1,80	0,7062	+10,44
0,5923	0,3	4809	3848	1,50	0,5885	—0,65
0,5923	0,5		3272	1,56	0,6121	+3,34

TABLE 3

Determination of Cobalt after Removal of Nickel

Taken, mg		Found, mg
Ni	Co	Co
5,8	0,5448	0,5534
6,7	0,6154	0,6193
7,6	0,6626	0,6584
8,8	0,7568	0,7536

The equivalence point was determined both graphically and analytically by the formula given in the work of Langer [3], and Alimarin and Gibalo [4].

The results given in Table 2 show that it is possible, in principle, to determine small amounts of cobalt by radiometric titration with potassium ferrocyanide using Co^{60} as indicator. In order to determine cobalt in a solution containing nickel, the latter was precipitated with dimethylglyoxime. A weakly acid solution containing nickel and cobalt salts was heated to the boil, a dimethylglyoxime solution was added, this was followed by sodium acetate until a precipitate was formed; some sodium acetate was then added in excess. The precipitate which settled out was centrifuged and washed, and the cobalt determined in the filtrate by radiometric titration.

As is evident fromTable 3, the results obtained in this case were satisfactory.

SUMMARY

By radiometric titration of small concentrations of cobalt ions with potassium ferrocyanide, it has been established that the composition of the precipitate formed corresponds to the formula $K_4Co_{10}[Fe(CN)_6]_6$.

The possibility has been demonstrated of determining small amounts of cobalt by radiometric titration with potassium ferrocyanide using Co^{60} as indicator.

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POLAROGRAPHIC DETERMINATION OF BERYLLIUM IN A SUPPORTING ELECTROLYTE OF TETRAETHYLAMMONIUM IODIDE

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The polarography of beryllium has been studied by Heyrovskii and Berezitskii [1]. It has been shown [2] that during electrolysis of solutions of beryllium sulfate or chloride two polarographic waves develop: the first is the hydrogen reduction wave at -1.48 volt, and the second is the reduction wave of beryllium at a potential of -1.84 volt. However, this wave is sharply deformed, it is not reproducible, and does not permit a sufficiently accurate and reliable determination of beryllium.

When tetramethyl- and tetraethylammonium salts are used as a supporting electrolyte a clearly defined polarographic wave is obtained for beryllium. Under these conditions the diffusion current is directly proportional to the beryllium concentration (Fig. 1).

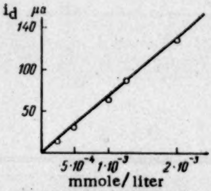

Fig. 1. Relation between the diffusion current and Be concentration. S = 1/100; supporting electrolyte 0.1 M $(C_2H_5)_4NI$; K = i_d/c = 70.

Since, on taking polarograms, beryllium salts give a current maximum, tetraethylammonium iodide (0.1 mole/liter), which can simultaneously suppress this maximum, was used as a supporting electrolyte. Measurements were made at a pH of 2.20-2.40. At higher pH values hydrolytic decomposition of the beryllium salts occur. The primary solution used was one of chemically pure beryllium sulfate; the concentration of the solution was $1 \cdot 10^{-2}$ mole/liter. Polarograms were taken over the range of concentrations $5 \cdot 10^{-4}$ to $2 \cdot 10^{-3}$ mole/liter. During these experiments the apparatus used was a visual polarograph, type M-7, of the Scientific Research Institute of Gorky University; it was provided with a galvanometer with an absolute sensitivity of $3.2 \cdot 10^{-9}$ amp/mm/meter (a); R_{internal} = 200 ohm; R_{cr} = 400 ohm. The distance of the center of the galvanometer mirror to the scale was 0.25 meter (1). The capillary constant was $m^{2/3} t^{1/2}$ = =2.148 mg $^{2/3}$ sec$^{-1/2}$ (m = 2.88 mg/sec, t = 0.7 sec). The shunting coefficient was b = 100. The temperature of the solution being polarographed was 19°. The diffusion current i_d was measured every 0.04 volt; a saturated calomel electrode was used as the external anode.

Conversion of the height of the polarographic wave $\underline{h}$, expressed in mm, into the diffusion current i_d in μ a, was carried out by a formula which we have given previously [3] (Fig.2).

The table contains results of measurements of the diffusion current as a function of the beryllium sulfate concentration.

As is evident from the results given in Table 1, the relation between i_d and beryllium concentration is only linear at low pH values of the solution (2.2-2.4 and lower). Above this limiting pH hydrolytic decomposition of beryllium salts occurs, and a solid phase is formed, as a result of which the diffusion current drops sharply; under such conditions i_d decreases to a greater extent the higher the pH (Table). This limiting hydrogen ion concentration at which a solid phase of $Be(OH)_2$ is formed depends on the concentration of the beryllium salt. Thus for a beryllium concentration of $2 \cdot 10^{-3}$ mole/liter, the pH at which a solid phase starts to appear is 2.35, while for a concentration of $1 \cdot 10^{-3}$mole/liter it is 2.5, and for $5 \cdot 10^{-4}$ the pH is 2.65,etc.

The Relation between the Diffusion Current and Beryllium Concentration ; S = 1/100, $m^{2/3} t^{1/6} = t^{1/6} = 2.148$ mg$^{2/3}$ sec$^{-1/2}$, pH 2.20-2.65

Initial beryllium concentration, mole liter	Height of the diffusion wave (h), μ a	Diffusion current (i_d) μa	pH of the solution	Initial beryllium concentration,	Height of the diffusion wave (h), μ a	Diffusion current (i_d), μ a	pH of the solution
$2 \cdot 10^{-3}$	106,0	135,0	2,20	$0,10 \cdot 10^{-3}$	5,4	6,9	2,20
$1,8 \cdot 10^{-3}$	96,5	124,0	2,20	$2,10^{-3}$	105,0	134,5	2,42
$1,5 \cdot 10^{-3}$	80,0	102,0	2.20	$2 \cdot 10^{-3}$	97,0	124,0	2,45
$1,25 \cdot 10^{-3}$	65,0	83,0	2,20	$2 \cdot 10^{-3}$	70,0	89,5	2,65
$1,20 \cdot 10^{-3}$	62,0	73,0	2,20	$1 \cdot 10^{-3}$	50,0	64,0	2,48
$1 \cdot 10^{-3}$	52,0	66,5	2,20	$1 \cdot 10^{-3}$	37,0	47,4	2,55
$0,8 \cdot 10^{-3}$	42,0	54,0	2,20	$1 \cdot 10^{-3}$	28,5	36,5	2,65
$0,6 \cdot 10^{-3}$	31,0	40,0	2,20	$0,5 \cdot 10^{-3}$	17,0	21,76	2,70
$0,5 \cdot 10^{-3}$	26,0	33,0	2,20	$0,5 \cdot 10^{-3}$	10,0	12,80	2,75
$0,25 \cdot 10^{-3}$	12,5	16,0	2,20	$0,5 \cdot 10^{-3}$	5,0	8,96	2,90

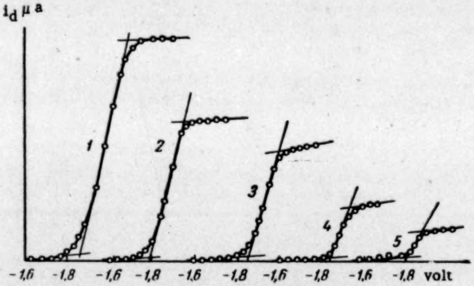

Fig.2. The relation between the diffusion current of beryllium sulfate and its concentration, in a supporting electrolyte of 0.1 M tetraethylammonium iodide. S = 1/100.
1) $2 \cdot 10^{-3}$ mole/liter Be; $i_d = 135$ μa, 2) $1.25 \cdot 10^{-3}$ mole/liter Be; $i_d = 83$ μa, 3) $1.0 \cdot 10^{-3}$ mole/liter Be; $i_d = 66.5$ μa, 4) $0.5 \cdot 10^{-3}$ mole/liter Be; $i_d = 33$ μa, 5) $0.25 \cdot 10^{-3}$ mole/liter Be; $i_d = 15.6$ μ a.

The table contains results of measurements of the diffusion current as a function of the beryllium sulfate concentration.

As is evident from the results given in the table, the relation between i_d and beryllium concentration is only linear at low pH values of the solution (2.2-2.4 and lower). Above this limiting pH hydrolytic decomposition of beryllium salts occurs, and a solid phase is formed, as a result of which the diffusion current drops sharply; under such conditions i_d decreases to a greater extent the higher the pH (table). This limiting hydrogen ion concentration at which a solid phase of $Be(OH)_2$ is formed depends on the concentration of the beryllium salt. Thus, for a beryllium concentration of $2 \cdot 10^{-3}$ mole/liter, the pH at which a solid phase starts to appear is 2.35, while for a concentration of $1 \cdot 10^{-3}$ mole/liter it is 2.5, and for $5 \cdot 10^{-4}$ the pH is 2.65, etc.

SUMMARY

Beryllium has been determined polarographically in a supporting electrolyte of tetraethylammonium iodide at a pH not higher than 2.2-2.4.

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AMPEROMETRIC TITRATION OF GALLIUM IN THE PRESENCE OF PHOSPHATE BY MEANS OF COMPLEXON III

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Determination of gallium in the presence of phosphate is connected with certain difficulties which are caused by precipitation of gallium phosphate on increasing the pH of the solution to about 2.7. This excludes the use of the usual gravimetric methods for the determination of gallium by precipitation of its hydroxide [1], and also excludes the photometric determination of gallium with quinalizarin (pH 5). Comparatively good results are obtained by the hydroxyquinoline method when one is working with a comparatively large amount of gallium (tens of milligrams). An indirect titrimetric method has been developed for the determination of gallium in the presence of PO_4^{3-} – the gallium is determined in the form of its complexonate using dithizone as indicator [2].

Amperometric Titration of Gallium with Complexon III in the Presence of 100-1000 times Its Amount of PO_4^3

Ga taken, mg	Ga* found, mg	Deviation	
		in mg	in %
39,79	39,80	+0,01	0,027
31,83	31,80	−0,03	0,094
23,87	23,89	+0,02	0,083
15,91	15,92	+0,01	0,062
7,96	7,95	−0,01	0,13
3,98	3,99	+0,01	0,25
2,39	2,38	−0,01	0,42
1,59	1,54	−0,05	3,1

*These values are the mean of three parallel determinations.

We have established that it is possible to determine gallium in the presence of phosphate by direct amperometric titration with Complexon III using the anodic current of the oxidation of the complexon at a potential of 0.8-1.0 volt (with respect to the saturated calomel half-element) [3]. The requisite potential was applied to the electrodes before immersing them in the test solution. The 0.1 M gallium chloride was established by the hydroxyquinoline method, while the 0.05 M Complexon III solution was standardized by titrating it with a zinc chloride solution using acid chrome blue as indicator.

Gallium is determined as follows: to a solution containing 1.5-40 mg of Ga and 100-1000 times its amount of PO_4^{3-}, is added HCl (1:1) until the precipitate of $GaPO_4$ has dissolved (pH about 1.5-2.5); the solution is diluted with water to 25 ml and is then titrated with 0.05 M Complexon III. The titrated with 0.05 M Complexon III. The titration curve has a L-shape. The increase in the current after the equivalence point is proportional to the concentration of excess complexon in the solution up to a concentration of about $2 \cdot 10^{-3}$-$3 \cdot 10^{-3}$ M/liter. On addition of more complexon the current changes slowly.

As the table shows, the method gives satisfactory results (mean experimental error < 0.5%) for a gallium content of 2.5-40 mg. A determination takes 10-15 minutes.

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DETERMINATION OF TELLURIUM IN LEAD-ANTIMONY-TELLURIUM ALLOYS

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The rapid and accurate method of determining tellurium in pure tellurium and in antimony-tellurium alloys [1] has proved unsuitable for alloys containing large amounts of lead, because of incomplete reduction of tellurium. In an alkaline medium, lead interferes with the reduction of tellurium by most of the known reducing agents.

We have found that tellurium can be quantitatively separated from lead and from most other elements by reducing it to the metal from a tartaric-nitric acid solution.

EXPERIMENTAL PROCEDURE

An aliquot, containing from 1 to 20 mg of tellurium is placed in a 150 ml conical flask fitted with a glass stopper. For each g of alloy, 2 ml of nitric acid (sp.gr. 1.4) and 3 ml of 30% tartaric acid are taken. Decomposition is carried out by gentle heating for 10 minutes. 10-20 ml of water is then added to the flask and the contents boiled for 2-3 minutes to remove nitrogen oxides. While still hot the solution is neutralized with 40% sodium hydroxide solution. During neutralization the lead hydroxide which is initially formed rapidly dissolves, while towards the end of neutralization it dissolves slowly even on shaking and heating the flask. It is important not to add excess sodium hydroxide. Neutralization is stopped when, on mixing and heating the solution to the boil, the small amount of flocculent precipitate of lead hydroxide starts to change into a heavy crystalline precipitate of lead tartrate. The amount of the latter should not exceed in volume that of 2-3 match heads. If, as a result of careless neutralization,, more lead tartrate than the amount indicated is formed, a few drops of nitric acid is added to dissolve this precipitate on heating, and the solution then neutralized carefully with sodium hydroxide.

After neutralization, a 20%, solution of stannous chloride is added dropwise, with stirring, to the solution which is heated almost to the boil; the stannous chloride is added until the tellurium has completely dissolved (as well as selenium, silver, gold, copper). After the solution has cleared, reduction of tellurium is carried to completion.

The supernatant liquid (after standing for 5-10 minutes) is filtered through a funnel fitted with a plug of glass wool and asbestos, endeavoring not to transfer any of the precipitate into the funnel. The filtrates are collected separately and completeness of reduction of tellurium checked again. The tellurium precipitate in the flask is washed by decantation 3-4 times with small portions of hot 30% ammonium acetate for removing lead from the precipitate, and then 3-4 times with hot 2% sodium sulfate solution; during this process the tellurium precipitate is almost completely transferred onto the funnel. The precipitate is only quantitatively transferred onto the funnel when the alloys contains gold.

After washing the precipitate, the stem of the funnel is washed from the outside and the liquid in it removed, the funnel and precipitate is placed in the neck of the flask in which reduction was carried out. 0.1-0.2 g of $NaNO_2$ is placed on the filter with the tellurium precipitate, the funnel is covered with a watch glass, and carefully, but rapidly, 2-3 ml of a mixture consisting of 2 ml of nitric acid (sp.gr. 1.4) and 3 ml of 30% tartaric

Taken, g					Tellurium found (in g) by:		
Pb	Sb	Cu	Se	Te	gravimetrically	titrimetrically with $K_2Cr_2O_7$, Mohr's salt, and diphenylamine	titrimetrically with $K_2Cr_2O_7$, H_2O_2, and $KMnO_4$
1,0	0,04	—	—	0,0347	0,0346	0,0345	0,0347
1,0	0,04	—	—	0,0174	0,0174	0,0172	0,0175
1,0	0,04	—	—	0,0035	0,0033	0,0034	0,0035
1,0	0,04	0,032	0,04	0,0347	—	—	0,0346
1,0	0,04	0,032	0,04	0,0174	—	—	0,0174
1,0	0,04	0,032	0,04	0,0035	—	—	0,0034

acid is introduced under the watch glass. A turbulent reaction occurs and the tellurium, after 1-2 minutes, dissolves; the solution is collected in the flask and the filter washed with HNO_3 (1:100). The funnel and plug can be used for subsequent filtering of the tellurium as long as the alloy does not contain gold.

The filtrate obtained is boiled for 2-3 minutes and then neutralized with 40% sodium hydroxide in the presence of phenolphthalein until the rose color of the latter is obtained; 6 drops of 40% sodium hydroxide is then added in excess and the solution heated; if, during this process, metallic silver separates out, the latter is filtered off through a funnel fitted with a plug of glass wool and asbestos, and the latter washed with 2% sodium sulfate solution. To the filtrate, depending on the copper content, is added 1 to 10 ml of 2N potassium ferrocyanide and 5 ml of a freshly prepared 20% solution of lactose, and the solution boiled for 15-20 minutes until the tellurium is completely coagulated; after standing, the solution is filtered through a funnel fitted with a plug of glass wool and asbestos. The precipitate is washed by decantation with 2% sodium sulfate solution (the precipitate is not quantitatively transferred onto the funnel on washing with the sodium sulfate).

The washed precipitate is washed back off the asbestos with a stream of water into the flask, the funnel with residual precipitate and the glass wool plug are placed in the flask; 10 ml of 4 N sulfuric acid is poured in small portions into the funnel, and 15 ml of 0.1 N potassium dichromate passed from a buret through the funnel in order to dissolve particles of tellurium adhering to the funnel.

After the particles of tellurium have been dissolved, the funnel is washed with what is left of the 10 ml of 4 N sulfuric acid and with water. The particles of tellurium adhering to the wall of the flask are washed off by means of the filtrate collected in the flask and complete solution of the tellurium is effected, as can be seen by the disappearance of the black particles of tellurium. The tellurium dissolves more rapidly on heating the flask to 50-60°. The solution is then cooled, and excess dichromate reduced with 0.1 N hydrogen peroxide, which is added from a buret at a rate of not more than 2-3 drops per second with continuous stirring. Titration with 0.1 N hydrogen peroxide is carried on until a pure green color is obtained; at this point a small excess of the standard solution is added. Excess of the latter is immediately titrated with 0.1 N potassium permanganate until there is a clearly defined change from green to lilac.

The amount of tellurium is calculated by means of the formula:

$$\%\mathrm{Te} = \frac{[(v_1N_1 + v_2N_2) - v_3N_3]\cdot 21.27\cdot 100}{1000\cdot n},$$

where v_1 and N_1 are the volume and normality of the potassium dichromate; v_2 and N_2 are the volume and normality of the potassium permanganate, v_3 and N_3 are the volume and normality of hydrogen peroxide, n is the weight of alloy taken.

Determination of tellurium in two samples, test and control, takes 2-3 hours.

When a test aliquot contains from 1 to 20 mg, the relative error lies within the limits 1 to 3% (Table).

Of particular importance is the fact that the titration end point is much more clearly defined than is the case in the titration with potassium dichromate and Mohr's salt using diphenylamine as the indicator. High results will be obtained on using hydrogen peroxide for reducing excess potassium dichromate only when the hydrogen peroxide solution is added rapidly without adequate stirring.

SUMMARY

A method which is comparatively accurate and rapid has been developed for the determination of tellurium in lead-antimony-tellurium alloys; the method has a titrimetric finish.

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DETERMINATION OF THE SULFOCHLORIDE NUMBER

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In order to obtain high molecular weight sulfonates, sulfamides, and sulfoethers of good quality by sulfochlorination of hydrocarbons, the reaction is stopped when 25-30% of the hydrocarbons has been converted into the sulfochlorides [1-4]. As a result of the chlorination side reaction which occurs at the same time, chlorinated hydrocarbons are formed; these, combined with unchanged hydrocarbons, constitute what is called the "reflux oil." The mixture of sulfochlorides, chlorinated hydrocarbons, and hydrocarbons – the so-called sulfonated mass then undergoes further treatment (saponification, amidation, esterification). Accordingly, it is necessary to know the sulfochloride content of the sulfonated mass. This can be accurately and simply expressed by the sulfochloride number (S.N); the following procedure is suggested for determination of this number.

A 1-1.5 g aliquot of the sulfonated mass which has been treated beforehand with an inert gas is rapidly weighed out on an analytical balance into a flask fitted with a ground glass stopper, and dissolved in 50 ml of an acetone-ether mixture (1:3). The solution obtained is titrated with an alcoholic solution of KOH, using a few drops of cresol red as indicator, to the appearance of a rose color which does not disappear in the course of 10-15 seconds. Then having added to the flask the same number of ml of the same alkali as was used for titrating to the first rose color, the flask is allowed to stand for 2 hours at room temperature.

After standing for two hours the solution is first titrated with hydrochloric acid (0.1 N) until the color changes from a purple-red to an amber yellow, it is then titrated with alcoholic KOH (0.1 N) until a purple-red color appears.

The sulfochloride number is determined in duplicate. At the same time one blank is carried out by direct titration with hydrochloric acid (0.1 N).

The sulfochloride number is calculated by means of the formula:

$$\text{Sulfochloride number} = \frac{(\alpha - \beta)T + \alpha' T'}{e}\left|\frac{\text{mg KOH}}{\text{g}}\right|,$$

where α is the number of ml of 0.1 N hydrochloric acid used for the direct titration in the blank experiment; α' is the number of ml of 0.1 N KOH used during the back titration in the test; β is the number of ml of 0.1 N hydrochloric acid used during the direct titration in the test; T is the factor of the 0.1 N hydrochloric acid with respect to KOH; T' is the factor of the 0.1 N KOH solution; and $\underline{e}$ is the weight of sample taken.

Knowing the sulfochloride number and the molecular weight of the sulfochloride, the sulfochloride content mass is readily calculated.

The method developed is characterized by its simplicity and accuracy, and by the cheapness of the reagents used. Neitzel's method [5] is not applicable in this case because the results obtained are high and are not reproducible. This can be explained by insufficient dispersion of the sulfonated mass, and by detachment of the chlorine from the chlorinated hydrocarbons of the sulfonated mass on heating to the boil, as recommended by Neitzel. By using a special mixture of solvents, and by leaving the reagents in contact with each other at room temperature, we were able to avoid these errors. The reproducibility of the results by the given method lies within the limits 98-99%, while the experimental accuracy is 97-97.5%.

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REVIEWS AND BIBLIOGRAPHY

THE ANALYTICAL CHEMISTRY OF INDIUM,
Monograph by A. I. Busev

(Izd. AN SSSR, Moscow, 1958)

The part played at present by the rare elements, in particular by indium, in science and technology has led to an intensive development of appropriate analytical methods. That such is the case is shown by the numerous papers which have appeared in recent years. In this connection therefore, the publication in 1958 by the Academy of Sciences of A. I. Busev's monograph "The analytical chemistry of indium" is very timely. In the monograph under review all the literature on methods of detecting, determining, and separating indium published through 1956 inclusively has been collected and carefully systematized.

In chapter 1 the author compares the most important qualitative reactions for the detection of indium, the essential methods for its quantitative determination, and the methods for separating it from interferring elements.

In the succeeding chapters the author gives a detailed description of the analytical methods of determining indium, the methods being arranged according to the reactions leading to the formation of the corresponding compounds, while they are classified according to the usually accepted method (i.e., gravimetric, titrimetric, photometric, etc.).

It should be pointed out, however, that such a classification may prove inconvenient, in the sense that it may be difficult to get a complete grasp of this or that analytical method, but, on the other hand, it has the advantage that it gives an exhaustive picture of the possibilities of the use of a certain reagent in the analytical chemistry of the given element.

In the monograph, the author not only touches upon existing methods of determining indium, but also gives complete chemical characterization of indium halides, the solubility and solubility product of its ferrocyanide and thiocyanate complexes, and the extractability of the bromide and other halide derivatives of indium by various organic solvents, etc.

Both Russian and foreign literature is made full use of in the monograph. The literature cited by the author has not been taken at random but has been critically chosen. On the basis of the published material, and on the basis of the author's personal experience in this field, the advantages and disadvantages of the analytical methods described are pointed out.

The published monograph is very useful, not only for specialists working with widely scattered elements, but also for a wide circle of chemists.

Yu. A. Chernikhov

A NEW REAGENT FOR GALLIUM

A new reagent for the luminescent determination of gallium has been synthesized in the All Union Scientific Research Institute of Chemical Reagents (IREA). The reagent is more sensitive and selective than acid chrome blue-black and sulfonaphtholazoresorcinol, while its inner-complex compound with gallium can be extracted with isoamyl alcohol. Using this reagent, gallium can be determined in the presence of 100 times its amount of aluminum. The reagent can also be used for preparing certain salts of particularly high purity (for purification of gallium from traces of aluminum, zinc, iron, copper, etc.).

Organizations and firms who wish to try the new reagent can get a free sample together with instructions for its use by applying to the following address: Moscow Zh-33, Samokatnaya Street, D. 4a, Institute of Chemical Reagents.

This reagent will be issued by the chemical industry under the name "Lumogallion IREA"; it can be obtained in any amount in the special shop of No.2 Trust "Soyuzreaktiv" (Moscow V-230, Warsaw Road, 135 a).

ANNOUNCEMENT

A conference on the analysis of rare and semiconductor elements will be held on December 7-11 in Moscow; this conference is convened by the Academy of Sciences USSR in conjunction with Gosplan USSR and GNTK of the USSR Soviet of Ministers.

The purpose of the conference is to discuss the present state, the outlook, and the problems of the analytical chemistry of rare and semiconductor elements, and will critically examine, systematize, and generalize the material available in research institutes and industrial laboratories on the analysis of lithium, beryllium, cesium, rubidium, scandium, yttrium, the rare earths, thorium, gallium, indium, thallium, silicon, germanium, titanium, zirconium, hafnium, vanadium, niobium, tantalum, molybdenum, tungsten, selenium, tellurium, and rhenium.

All those who wish to participate in the work of the Conference should write to the Organizing Committee at the following address: Moscow, Vorobevskii Road, 47a. Tel. V-2-05-08 Ext. 52, 1-23.

Organizing Committee

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THE EFFECT OF THIRD ELEMENTS DURING SPARK SPECTROGRAPHIC ANALYSIS OF SOLUTIONS

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State Scientific Research and Design Institute of the Rare
Metal Industry, Moscow

The advantages of spark spectrographic analysis of solutions are well known. In many cases in the analysis of solid materials it is expedient to get them into solution beforehand [1-11]. During spark excitation of the spectrum, a change in the composition of the solutions is often accompanied by a change both in the absolute and in the relative intensities of the lines of the elements (the effect of "third elements", anions, etc.) which leads to the appearance of systematic experimental errors [1, 5-8, 15, 17, 20, 26, 27, 32]. However, most published material on the spark analysis of solutions is devoted, in the main, to a choice of conditions for carrying out the determination. Information on the mechanism of the passage of the solutions into the discharge zone, about the effect of changes in the composition of the solutions on the excitation conditions of the spectra, and about the mutual effect of elements on line intensity is very limited.

It should be mentioned in this connection that usually a spark discharge between the surface of the solution and a solid electrode is used [1-4, 8, 11-17, 19-23, 28]; in many cases the solutions are evaporated on the electrode surface, and the film of salts covering the electrode is subjected to the action of the spark [9, 10, 24, 25, 27, 29, 30].

In the latter instance the conditions under which the elements diffuse into the surface layer of the material [2], and the changes in its composition under the influence of the spark discharge [18] affect the line intensity.

The present article describes an attempt to establish the relationship of line intensity to the properties of solutions, and of line intensity to the mutual effect of the elements. The relationships were examined under two sets of conditions, the first set of conditions excluding as much as possible the effects of processes occurring on the electrodes (formation of a discharge directly between the two surfaces of the solutions), the second set of conditions allowing us to expect that these processes occurring on the electrodes would show up quite clearly.

1. Apparatus, Spectrum Excitation Source, and Methods of Introducing the Solutions into the Spark Discharge Zone.

The spectrum excitation source was an IG-2 spark generator which is included in a Raiskii setup [31]; in the latter the breakdown voltage in the operating spark gap depends only to a very small extent on the distance between the electrodes and the state of the electrode surface, and is applied by means of an additional spark discharger.

The solution was introduced into the spark gap both by means of rotating disc electrodes [13, 14], and by means of a capillary electrode [16]. Two discs made from graphite or red copper, 39 mm in diameter and 5 mm thick, were fitted up as shown in Fig. 1 at a distance of 3.5 mm from each other. By choosing the rate at which the discs rotate, conditions are established for forming a discharge immediately between the surfaces of the solution covering the discs. The rate at which the discs were rotated (within the limits of 3 to 100 rpm) was regulated by means of a reducer connected to the motor.

When the solution was introduced by means of a capillary graphite electrode, the graphite fulgurator shown in Fig. 2 was used. The electrode, which was made from spectrographically pure carbon, was in the form of a cylinder 8 mm long and 5.5 mm in diameter, and had a hole 3.5 mm in diameter bored along its axis. It was fitted in a massive graphite beaker 2.

By means of a plexiglas mold fitted on top of the fulgurator's beaker, the cylindrical electrode was always kept in a position so that its end stuck out 3 mm above the edges of the beaker.

In order to overcome the porosity of the graphite beaker of the fulgurator, the latter, after it had been prepared, was immersed in a solution of plexiglas in chloroform.

The test solution, 3.5 ml in volume, was placed in cavity 3 of the fulgurator beaker; the fulgurator was placed on the metallic surface of the lower electrode; the upper electrode which was a pointed carbon electrode 4 was fixed in a retort clamp above the cylindrical electrode at a distance of 3.5 mm.

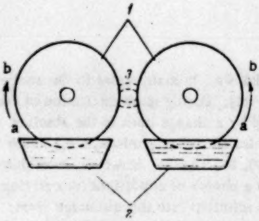

Fig. 1. Introducing the solution into a spark discharge on rotating electrodes. 1) Rotating copper or graphite discs; 2) solution; 3) spark discharge.

The solution placed in the fulgurator rises in the electrode canal and covers the electrode surface with a fine film; when the surface of the cylinder is subjected to the spark discharge, the thin film of liquid covering it is continuously renewed by passage of fresh portions of solution from the electrode canal [16]

The use of a massive graphite fulgurator prevented the warmup of the solution during the period of the spark discharge.

Conversion from line blackening on the photographic plates to line intensity was carried out by the usual method, using the characteristic curves of the photographic plate, these curves being obtained for each plate. Corrections for background intensity were then applied to the values found for the line intensity.

The apparatus and the operating conditions used for getting the spectra are given below:

Spectrograph	Quartz, ISP-22
Linear dispersion	6.5-45 A/mm
Spectral region	2350-4550 A
Photographic plates	Spectrographic, Type II, sensitivity 16 GOST units
Spectrum excitation source	IG-2 sparkformer, included in a Raiskii setup (2 amp, 220 v) capacity of 0.01 microfarad; self-inductance 0.15 millihenries
Disc electrodes	Graphite or copper; 39 mm diameter, 5 mm thick
Rate of rotation	3-100 rpm
Spark gap	3.5 mm
Exposure time (time for which spectra were photographed)	30-180 sec
Capillary electrode	Graphite; 8 mm long; 5.5 mm diameter; diameter of its hole 3.5 mm
Spark gap	3.5 mm
Exposure time	40-180 sec

2. Introducing the Solution into the Discharge Zone on Rotating Electrodes

During the formation of a spark discharge on the surface of a liquid contained in a cup-shaped metallic electrode of the Gerlach type [28], the line intensity of the elements present in the solution is usually low; when this type of electrode is used, a strong sputtering of the solution is observed and this leads to difficulties in carrying out a determination.

Satisfactory conditions for evaporating the solution in a spark discharge as well as a sharp increase in the line intensity of the spectra are observed on introducing a thin film of the solution into the discharge zone by means of rotating electrodes [4, 13-15], or by means of cylindrical electrodes with a central opening. These electrodes are immersed in the test solution, and as a result of capillary phenomena, the opening in the electrodes is covered with a layer of solution [5-7, 11, 16, and 21].

Attempts to measure the film thickness of a solution introduced into a spark were made by Effendiev [8]; the method which he adopted for measuring the film thickness on an immersed electrode could not, however, guarantee that the true thickness of the solution was being measured.

It was found that it is possible to make a sufficiently accurate determination of the film thickness and to establish the effect of this film thickness on line intensity by introducing the solution on the rotating discs shown in Fig. 1.

The amount of solution introduced into the discharge zone was determined from the increase in weight of a wad of filter paper which was pressed onto the edge of the disc to wipe its surface dry. When working with discs, precautions were taken so that the solution did not rise from the side walls onto the disc surface while it was being wiped with the filter paper wad. The film thickness on the disc surface was calculated by means of the formula: $d = g/2\pi rla$, where d is the film thickness; r is the radius of the disc; l is the thickness of the disc; g is the weight of solution collected during one revolution of the disc; and a is the specific gravity of the solution.

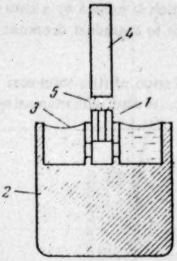

Fig. 2. Introducing the solution into a spark discharge from a capillary electrode. 1) Cylindrical graphite electrode; 2) graphite fulgurator; 3) solution; 4) upper electrode; 5) spark discharge.

The film thickness on the part of the disc which rises into the spark discharge, other conditions being equal, depends on the runoff time of the liquid from the surface of the disc rising upward, and, consequently, not only on the viscosity of the solution, but on the rate at which the disc is rotating; increasing the rotational rate leads to an increase in the film thickness on the disc surface. In measuring the film thickness one should remember that the film thickness of the withdrawing layer of liquid rapidly decreases on going from point *a* to point *b* in Fig. 1; subsequently, the liquid runoff stops and after point *b*, changes in the film thickness come to a stop. Accordingly, all measurements of the film thickness should be carried out on those parts of the disc coming after point *b*.

TABLE 1

The Relation of the Blackening of the Cd line I 3261.1 to the Nature of the Anion (Concentration of Cd in solution 0.5%)

Salt	Blackening of the Cd line 3261.1			
	capillary graphite electrode	rotating electrode		graphite electrodes covered with a solid film of the salt
		graphite	copper	
$CdSO_4$	1.12	0.94	0.43	1.01
$CdCl_2$	1.12	0.91	0.44	1.22
$Cd(NO_3)_2$	1.15	0.96	0.43	1.17
$Cd(CH_3COO)_2$	1.13	0.98	–	1.12

The film thickness depends to a considerable extent on the state of the disc surface; accordingly, in each case, before measuring the film thickness of solutions, the surfaces of the discs were submitted to a fairly long preliminary treatment by a spark discharge in order to remove accidental contamination, and to enhance the wettability of the disc by the solution. The relation between the thickness of a water film and the runoff time of the liquid as the disc moves from point a to boint b, a relation which is characteristic of graphite and carbon electrodes, is shown in Fig. 3. An increase in the runoff time of the liquid, which is caused by a slowing down in the rotational rate of the disc, leads to a gradual decrease in film thickness.

In Fig. 4 is shown, as an example, the relation of film thickness to the number of revolutions per minute of a graphite disc; with increasing rotational rate of the disc there is observed a gradual slowing down of the growth of the film thickness.

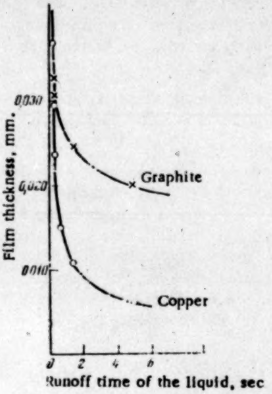

Fig. 3. Relation of the film thickness of water on graphite and copper discs to the runoff time of the liquid.

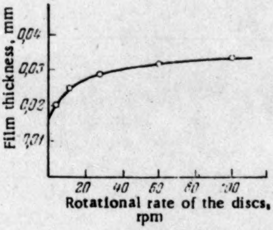

Fig. 4. Relation of the film thickness of water to the rotational rate of graphite discs.

Changes in the value of the film thickness with changes in the composition of the test solution for the case of aqueous solutions of sulfuric and hydrochloric acids, using graphite and copper discs, are shown in Fig. 5. In all these cases the film thickness was measured for discs rotating at a rate of 20 rpm.

From a consideration of Fig. 5, it is clear that the film thickness of a solution introduced into the spark discharge zone increases appreciably on increasing the concentration of hydrochloric and sulfuric acids, and tends to some constant value. As is evident from Fig. 6, it increases with increasing viscosity of the solutions. From Fig. 7, it is clear that the temperature of the solution, which alters its viscosity, also affects the film thickness; thus, a change in temperature of the solution from 0 to 80° leads to a drop of four times in the film thickness (i. e., the film thickness at 80° is one quarter of that at 0°) of water when copper electrodes rotating at 20 rpm are used. The relation between the film thickness of water and its viscosity is shown in Fig. 8.

During the spark analysis of solutions using rotating electrodes, it is usual to deal with film thicknesses within the limits of 0.006-0.06 mm; the amount of solution introduced in unit time into the discharge zone usually changes within the limits of 0.2 to 6.0 mg/sec.

The amount of solution evaporated in the discharge zone on introducing the solution on a rotating disc was measured on the basis of the weight of solution passing into the spark and that remaining on the disc after it has passed through the spark discharge; at the same time the thickness of the film of solution remaining on the disc was determined. Experiments showed that an increase in the rotational rate speed of the electrode, which leads to an increase in the film thickness of the solution, and, consequently, to an increase in the amount of solution introduced into the discharge, is accompanied by an increase in the amount of solution used up in the discharge zone. In the case of copper discs this is illustrated by (Curve 1 in Fig. 9).

Figure 10 makes it possible to view the change in the film thickness on the disc before and after the solution has passed through the spark discharge as a function of the rate at which the disc rotates. The film thickness,

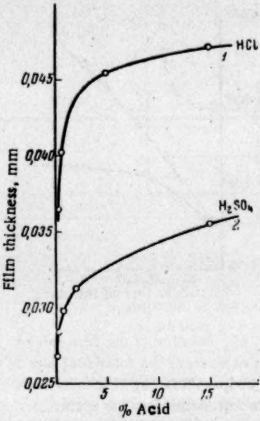

Fig. 5. Relation of the film thickness of a solution to the sulfuric and hydrochloric acid concentrations of the solution. 1) Graphite disc; 2) copper disc.

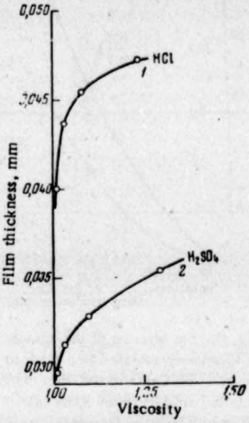

Fig. 6. Change in film thickness on graphite discs with increasing viscosity of the solution. 1) Graphite disc; 2) copper disc.

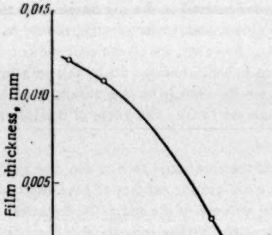

Fig. 7. Change in film thickness as the temperature changes, using copper electrodes.

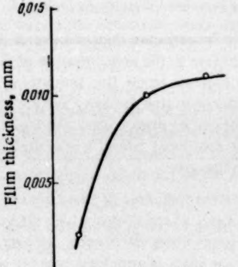

Fig. 8. Relation of film thickness to the viscosity of water, using copper electrodes.

and, consequently, the amount of solution remaining on the disc surface, are approximately constant and only depend to a very small extent on the amount of solution introduced into the discharge.

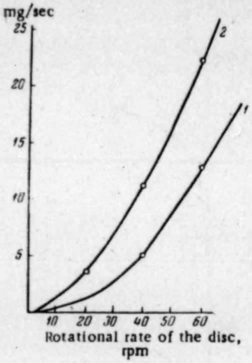

Fig. 9. The relation of the amount of solution evaporated in a spark to the rotational rate of the disc. 1) Solution used up in the spark discharge; 2) solution introduced into the spark discharge.

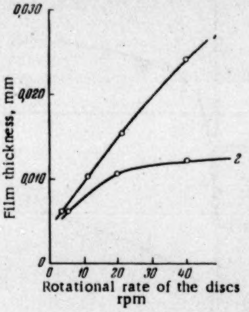

Fig. 10. Relation of the film thickness of water to the rotational rate of the the copper discs. 1) Thickness of the film introduced into the spark; 2) thickness of the film after it has passed through the spark.

3. Relation of Line Intensity to Film Thickness; Relation of Line Intensity to the Amount of Solution Introduced into the Discharge

In order to establish the relation of line intensity to film thickness, and to amount of solution evaporated in a spark discharge, the spectra given by the central part of the spark discharge (for various values of the film thickness and amounts of solutions used up in the discharge zone) were photographed.

It might be expected that an increase in the weight of solution evaporated in the discharge zone should lead to an increase in the concentration of the elements in the spark cloud, and, consequently, should be accompanied by an increase in the line intensity of the elements in solution. However, measurements showed the opposite relation between line intensity and the amount of solution used up in the discharge zone; this relationship for the case of copper discs is shown in Fig. 11. In Fig. 12 is also shown the change in line intensity on gradually increasing the rotational rate of a graphite disc, which leads to an increase in film thickness of the solution introduced into the spark.

The relation indicated of line intensity to film thickness, and to the rotational rate of the disc holds not only in those cases where spectra given off by the central part of the spark are the subject of investigation, but also in those cases where the spectra are averaged for all the radiating volume of the spark; in the latter instance, the image of the spark is projected onto the plane of the spectrograph prism, taking into account the possibility of displacement of the spark along the electrode surface.

The noncorrespondence observed between the amount of solution evaporated in the spark discharge and the intensity of the emitted lines of the elements cannot be ascribed to possible changes in the excitation conditions in the spark discharge. This was proved in the following manner. Small amounts of iron salts were added to test solutions containing 0.01% Cr, 0.001% Zr, and 0.2% Pb, and the relative intensity of the spark and arc lines of iron Fe II 2739.6 and Fe I 3047.6 were noted. These lines, sensitive to any changes in excitation conditions, as is shown in Figs. 11 and 12, indicated no appreciable or systematic breakdown when the film thickness or the amount of solution introduced into the spark discharge is altered.

The drop in intensity, without exception, of all the lines of the elements in solution is most readily explained by a deterioration in the conditions of the passage of the evaporating element into the discharge, on increasing the film thickness.

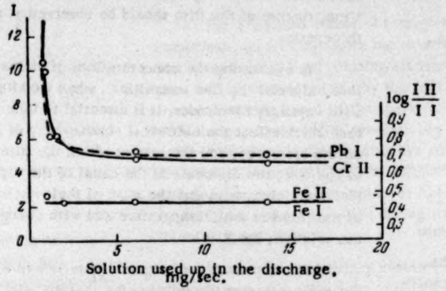

Fig. 11. The relation of the absolute intensity of lead and chronium lines and the relative intensity of the arc and the spark lines of iron to the amount of solution evaporating in a spark discharge.

For fairly large film thicknesses, the passage of a solution in the discharge has the character of an explosion, during which most of the evaporating solution is directed towards the edge of the spark cloud. It should be noted that the increase in line intensity with decreasing film thickness is always accompanied by rupture of the film by the spark, this rupture leaving clear traces on the disc surface.

On the other hand, a sharp decrease in line intensity is observed when a fairly thick film which is not ruptured by the spark forms on the surface of the disc; a further increase in film thickness is accompanied by a comparatively small weakening of line intensity. The value of the "critical" film thickness which can be ruptured by a spark depends on the composition of the solutions, and is usually of the order of thousandths of a millimeter.

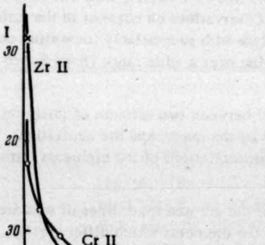

Fig. 12. The relation of the line intensity of zirconium and chromium to the rotational rate of graphite discs.

The constancy of the excitation conditions when working with films of variable thickness makes it possible, as a first approximation, to assume that the ratio of the line intensities I_1/I_2 for various values of the film thickness of a solution is proportional to the ratio of the amounts of the solutions actually passing into the spark cloud. In this case I_1/I_2 is approximately equal to a_1g_1/a_2g_2, where g_1 and g_2 are the total amounts of solution used up in the spark; and a_1 and a_2 are correction factors which determine the efficiency of the entry of the solutions into the spark zone.

Calculations have shown that the efficiency coefficient $A = a_1/a_2$ always sharply decreases with increasing film thickness of a solution passing into a spark discharge; the decrease in the value of the efficiency coefficient with increasing film thickness of a solution is shown in Fig. 13 in a case where copper discs were used.

Other conditions being equal, the efficiency with which a solution is used up depends to a very large extent on its electrical conductivity; an increase in the latter makes it difficult for the film to be ruptured by a spark discharge. The capacity of a spark to rupture

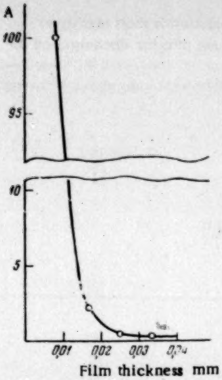

Fig. 13. The relation of the efficiency coefficient of a solution evaporating in a spark to film thickness on a rotating copper electrode.

a film depends to a very large extent not only on the film thickness and its electrical conductivity, but also on the rate at which it is introduced into the spark on the surface of the rotating disc; a drop in the speed of the disc not only leads to a decrease in film thickness, but also to an increase in the time for which it stays in the discharge zone, the latter facilitating rupture of the film by the spark. Accordingly, on switching from rotating electrodes to capillary electrodes in which the film is renewed for a longer time, rupture of the film should be observed at significantly larger film thicknesses.

In evaluating the concentrations of elements on the basis of the absolute values of the line intensities when working both with rotating and with capillary electrodes, it is essential to take into account all those factors which affect the electrical conductivity of a solution, the film thickness on the electrode, and the rate at which the film is renewed (the rotation rate of the disc, the diameter of the canal of the capillary electrode, the material of the electrodes and the state of their surfaces, the change in viscosity of the solution with temperature and with changes in the composition of the solution, etc.).

The appearance of organic materials in solution as a result of chemical preparation of the solution for analysis, and the changing viscosity of solutions and their capacity to wet the electrodes should also be taken into account during the spark analysis of solutions when capillary and rotating electrodes are used. For example, the gradual addition of sugar to a solution, which increases the viscosity, leads to a continuous drop in line intensity when using capillary graphite electrodes. This results from the slowing down of the rate of renewal of the film (Fig. 14).

4. The Effect of Third Elements on the Excitation Conditions during the Spark Analysis of Solutions.

One of the possible causes of the effect of third elements on the line intensity of the elements under observation may be a change in the excitation conditions in the spark cloud, caused by the appearance in the solution of foreign elements and particularly of elements with low ionization potentials.

The breakdown in the excitation conditions during the spark analysis of solutions was established from the change in the relative intensity of the spark and arc lines of iron Fe II 2739.6 and Fe I 3047.6; iron was introduced into all the test solutions as a chloride; the concentration used was 0.01%. Observations on changes in the ratio of the intensities of the iron lines indicated were made on a series of solutions with successively increasing concentrations of the interfering elements which had ionization potentials varying over a wide range (from 3.9 to 14.5 ev).

It was found that in those cases in which the spark discharge is formed between two surfaces of fairly thick films of solutions on rotating disc electrodes, the films are rarely punctured by the spark, and the excitation conditions depend only slightly on the ionization potentials or the atomic concentrations of the elements introduced into the solution.

This is very clearly shown in Fig. 15 in which the relative intensity of the arc and spark lines of iron are plotted along the ordinate, while the values of the atomic concentration of the elements which differ greatly from each other in their ionization potentials are plotted along the abscissa.

When the rotational rate of the electrodes is slower and the thickness of the film of solution decreases, the effect of elements present in solution on the relative intensity of the spark and arc lines of iron becomes more and more clearly marked. This can be seen for example on comparing the curves shown in Fig. 16 which relate the relative intensity of the arc and spark lines of iron to the potassium concentration in solution, when solutions are introduced into the discharge in the form of thick and thin films. In the latter instance, the drop in the relative intensity of the lines of iron indicated shows up quite clearly for only 0.1 g atom/liter of the potassium (0.5% potassium) in solution.

The effect of the elements' ionization potential and of the concentration of the elements on the relative intensity of the arc and the spark lines of iron shows up clearly on switching from paired disc electrodes (Fig. 1) to a capillary electrode (Fig. 2), in which the film of solution is readily punctured by the spark.

The enhanced effect of foreign elements on the excitation conditions, on slowing down the rotational rate of the electrodes and on switching from rotating electrodes to capillary electrodes presumably, is determined by the fact that, in this case, the current-conducting canal of the spark coincides to a lesser extent with the gas cloud of the spark giving off the light. The phenomenon of the drop in the dependence of the spark temperature on the ionization potential of the third elements when the spark canal and the gas cloud do not coincide has been observed, for example, by Feldman and Wittels [19] during work with a porous electrode filled with solution.

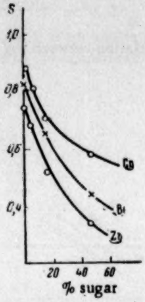

Fig. 14. Changes in blackening of the lines Cd I 3261.1, Zn I 3345.0, and Be 3321.3 on increasing the sugar concentration in a solution, using a graphite capillary electrode. Concentrations: 0.5% Cd, 0.05% Zn, and 0.005% Be.

In work with capillary electrodes the appearance in solution of large concentrations of elements with high ionization potentials has no effect on the relative intensity of the arc and spark lines of iron (Fig. 17). On gradually switching over to elements with lower ionization potentials, there is observed a more and more significant increase in the relative intensity of the arc and spark lines and this appears at lower and lower concentrations of elements in the solution.

Thus, in a spark discharge there is clearly manifested a change in the ratio of the intensities of the lines of elements, which is also characteristic for an arc discharge, in which the appearance of elements with low ionization potentials leads to a drop in the temperature conditions of excitation [33, 34].

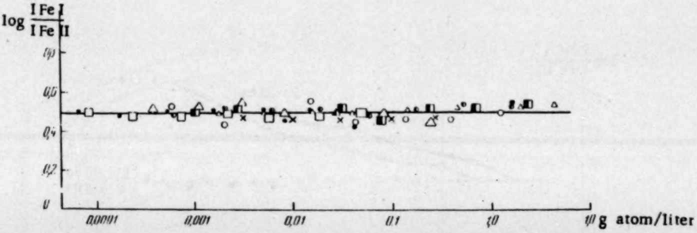

Fig. 15. The relation between the relative intensity of the lines Fe I 3047.6 and Fe II 2739.6 and the atomic concentrations of elements with varying ionization potentials; graphite rotating electrodes ☐ Cs 3.9 ev; ● Ca 6.1 ev; △ Zn 9.4 ev; △ Cl 12.9 ev; ○ K 4.3 ev; × Cu 7.7 ev; ○ S 10.6 ev; ☐☐ N 14.5 ev.

As an example, there is given in Fig. 18, for the case of a capillary graphite electrode, the relation of the relative intensity of the arc and spark lines of iron to the ionization potential of the elements for constant values of the atomic concentrations of the elements in solution. From Fig. 18 for example, it is clear that for each atomic concentration of the elements, there exists some minimum value of the ionization potential above which the elements present in solution do not affect the relative intensity of the arc and spark lines of iron Fe I 3047.6 and Fe II 2739.6. A further drop in the ionization potential causes a very sharp decrease in the value of the relative intensity of the lines indicated. A simple relation, (Fig. 19, Curve 1) exists between the minimum atomic concentration of an element in solution, above which the element starts to affect the relative intensity of the lines, and the value of the ionization potential E of the element.

The relation indicated can be expressed by $C = aE^b$, so that, for example, the relation between log C and log E (Fig. 20) is linear.

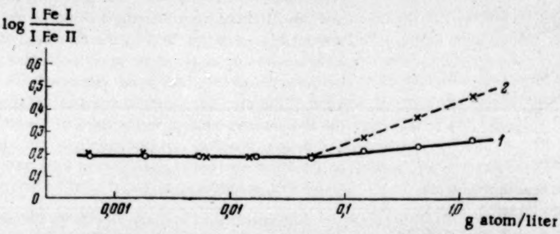

Fig. 16. The relation between the relative intensity of the arc and spark lines of iron and the atomic concentration of potassium in solution, for various rotational speeds of a disc electrode. 1) 11 rpm; 2) 3 rpm.

As pointed out already, on switching from a discharge between two fairly thick films of solution on rotating electrodes, to a discharge between a graphite electrode covered with a film, which has a graphite electrode fitted above it, there is observed a sharp increase in the effect of the elements on the relative intensity of the arc and spark lines. Accordingly, on switching to a discharge between two carbon electrodes covered with a solid film of the salts of the elements, one might expect an increase in the effect of the elements on the relative intensity of the lines Fe I and Fe II. Experiments confirmed such an assumption. The effect of constant amounts of potassium on the relative intensity of the lines FeI/Fe II continuously increases on switching from rotating discs to capillary electrodes, and then on to dry electrodes covered with a film of potassium salts (Fig. 21). For greater reliability,

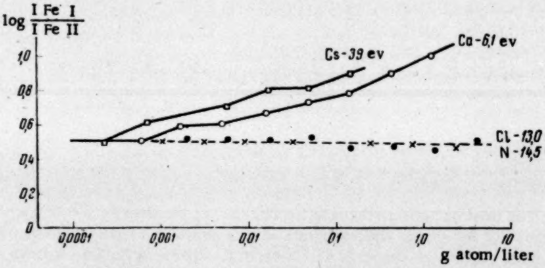

Fig. 17. The relation between the relative intensity of the iron lines Fe I 3047.6 and Fe II 2739.6 and the atomic concentration of elements with varying ionization potentials on introducing the solution into a spark between graphite capillary electrodes.

the initial values of the relative intensity of the lines Fe I and Fe II were commensurable for the methods indicated of introducing the solutions into a spark discharge.

During spark analysis of solutions of variable composition, elimination of systematic errors caused by changes in the concentrations of the elements and the composition of the solution, depends to a very large extent on the homology of the analytical lines; the demand for homology of the lines should increase on switching from a discharge formed between two rotating discs to a rotating disc with a stationary upper electrode, and, particularly to a capillary electrode.

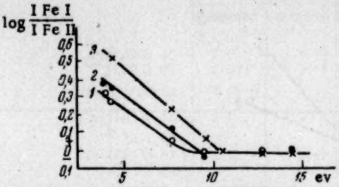

Fig. 18. The relation of the relative intensity of the iron lines Fe I 3047.6 and Fe II 2739.6 to the ionization potential of the elements when introducing the solution into the spark from a capillary graphite electrode: 1) 0.1 g atom/liter; 2) 0.25g atom/liter; 3) 1.0 g atom/liter.

When lines which are sharply nonhomologous are used, e.g., those consisting of spark and arc lines of the elements, the systematic experimental errors obtained during the determination of elements on the basis of calibration curves constructed within the coordinates log C and log (I_1/I_2), may, when one uses a capillary electrode, sometimes become as high as 200%, in those cases where the solution may contain a few percent of alkali metal salts which extinguish the spark lines of the elements.

It should be pointed out that in addition to the clearly manifested dependence of the relative intensity of a sufficiently homologous pair of lines on the ionization potentials and on the concentrations of the elements present in solution, there has also been observed, but to a lesser degree, a more complex breakdown in the ratio of the intensities of the lines when third elements are present in solution. This latter shows up clearly, for example, in those cases where elements with high ionization potentials, but which do not affect the excitation conditions in a spark discharge, are introduced into the solution. Thus, on gradually increasing the atomic concentration of zinc (9.4 ev)

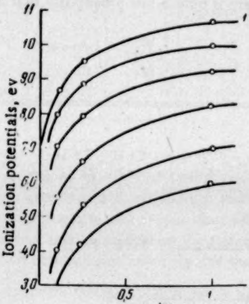

Fig. 19. Values of ionization potentials and atomic concentrations of the elements which lead to equal changes in the ratio of the intensities of the lines Fe I 3047.6 and Fe II 2739.6. The solution was introduced into the spark from a capillary graphite electrode.

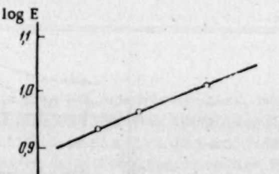

Fig. 20. Values of the ionization potentials and atomic concentrations of the elements which lead to equal changes in the ratio of the intensities of the lines Fe I 3047.6 and Fe II 2739.6. The solution was introduced into the spark from a capillary electrode.

as zinc nitrate in solution, there was observed a corresponding gradual change in the relative intensities of the lines of the elements present in solution (Fig. 22); at the same time, no changes in the relative intensity of the spark and arc lines of Fe I and Fe II, which react to changes in the excitation conditions of the spectrum, were observed. Attempts to connect these phenomena with such factors as the atomic weight of an element, whether the lines belong to neutral or ionized atoms, the excitation potentials of the lines, the reabsorption of the lines, etc., did not lead to any definite results.

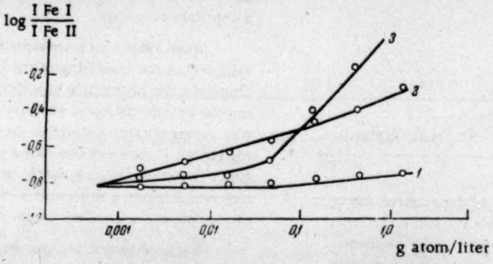

Fig. 21. The relation between the relative intensity of the arc and spark lines Fe I 3047.6 and Fe II 2739.6 and the atomic concentration of potassium in solution. 1) Solution introduced on rotating graphite electrodes; rotational rate 11 rpm; 2) solution introduced from a capillary graphite electrode; 3) solution evaporated on the surface of a graphite electrode.

The breakdown in the ratio of the intensities of the lines, which is not related in a definite way to changes in the excitation conditions in the spark cloud, usually only manifests itself at fairly high concentrations of the interfering element, sometimes exceeding by several orders the concentration of the test element.

Preliminary results which we have obtained indicate that there is only a low probability that anions affect intensity of the lines of the elements.

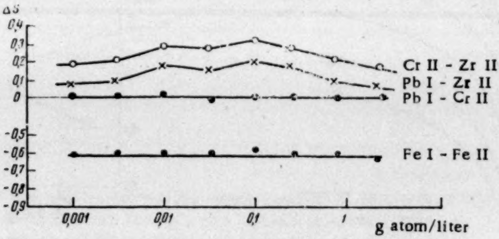

Fig. 22. Relation between the difference in blackening of the lines and atomic concentration of zinc as $Zn(NO_3)_2$ in solution; Cr II 2677.2 Pb I 2802.0 Zr II 2571.4, Fe I 3047.6 and Fe II 2739.6.

TABLE 2

Sensitivity of the Determination of Elements during Spark Analysis of Solutions

Lines	Conc. of elements in sol. in which its line appears, %		
	rotating electrode		capillary graphite electrode
	graphite	copper	
Ca II 3968,47 II 3933,67	$1\cdot10^{-6}$ $1\cdot10^{-6}$	$1\cdot10^{-6}$ $1\cdot10^{-6}$	$1\cdot10^{-6}$ $1\cdot10^{-6}$
Mg II 2795,53	$3\cdot10^{-6}$	—	$3\cdot10^{-6}$
Be II 3130,42	$3\cdot10^{-6}$	$1\cdot10^{-6}$	$3\cdot10^{-6}$
Zr II 3391,98 II 3438,41 II 3496,21	$5\cdot10^{-6}$	$3\cdot10^{-5}$	$1\cdot10^{-6}$
II 2568,87 II 2571,39 II 2678,63	$3\cdot10^{-6}$	$3\cdot10^{-5}$	$1\cdot10^{-5}$
Cu I 3273,96 I 3247,54	$1\cdot10^{-5}$	—	$1\cdot10^{-5}$
Mn II 2605,69 II 2593,73 II 2576,10	$3\cdot10^{-5}$	$1\cdot10^{-4}$	$1\cdot10^{-5}$
Sr II 4077,71	$3\cdot10^{-5}$	—	$3\cdot10^{-5}$
Mo II 2816,15	$3\cdot10^{-5}$	$3\cdot10^{-5}$	$3\cdot10^{-5}$
II 2848,23 II 2871,51	$3\cdot10^{-5}$	$1\cdot10^{-4}$	$1\cdot10^{-4}$
Ti II 3349,04	$3\cdot10^{-5}$	$1\cdot10^{-3}$	$3\cdot10^{-5}$
II 3341,88 II 3372,80	$1\cdot10^{-4}$	$1\cdot10^{-3}$ $1\cdot10^{-3}$	$1\cdot10^{-4}$ $3\cdot10^{-4}$
II 3088,03	$3\cdot10^{-4}$		
Fe II 2761,81 I 2750,14 II 2739,55 II 2599,40	$5\cdot10^{-5}$	$1\cdot10^{-4}$ $2\cdot10^{-4}$ $3\cdot10^{-4}$ $1\cdot10^{-4}$	$1\cdot10^{-4}$
Ag I 3382,89 I 3280,68	$3\cdot10^{-5}$		$1\cdot10^{-4}$
Cr I 4254,35	$3\cdot10^{-4}$	$2\cdot10^{-4}$	$1\cdot10^{-4}$
Al I 3961,53	$2\cdot10^{-4}$	$1\cdot10^{-4}$	$3\cdot10^{-4}$
B I 2497,73 I 2496,78	$1\cdot10^{-4}$	$1\cdot10^{-4}$	$1\cdot10^{-4}$
Nb 2950,88 2941,54 2927,81	$1\cdot10^{-7}$	$5\cdot10^{-4}$	$3\cdot10^{-4}$
Ta 2512,04	$1\cdot10^{-4}$	$1\cdot10^{-4}$	$1\cdot10^{-4}$
Co I 3453,5	$1\cdot10^{-3}$	$3\cdot10^{-3}$	$3\cdot10^{-4}$
Ni I 3414,77 II 2416,14	$3\cdot10^{-3}$	$3\cdot10^{-3}$	$1\cdot10^{-3}$ $5\cdot10^{-4}$
Tl I 3519,24	$5\cdot10^{-4}$	$3\cdot10^{-3}$	$1\cdot10^{-3}$
Y II 3710,29 II 3216,68	$3\cdot10^{-4}$ $1\cdot10^{-3}$	$1\cdot10^{-3}$ $3\cdot10^{-3}$	$1\cdot10^{-4}$ $5\cdot10^{-4}$
Ba II 4554,04	$5\cdot10^{-5}$	$1\cdot10^{-3}$	$2\cdot10^{-4}$
W I 2946,98 I 2944,40	$2\cdot10^{-3}$ $2\cdot10^{-3}$	$5\cdot10^{-4}$ $5\cdot10^{-4}$	$3\cdot10^{-3}$ $3\cdot10^{-3}$
Ga I 4172,06	$3\cdot10^{-4}$	$3\cdot10^{-4}$	$1\cdot10^{-3}$
Sb I 2528,54 I 2598,06	$3\cdot10^{-4}$ $5\cdot10^{-4}$	$3\cdot10^{-3}$ $3\cdot10^{-3}$	$3\cdot10^{-4}$ $1\cdot10^{-3}$
In I 3256,09 I 3039,36	$1\cdot10^{-3}$ $5\cdot10^{-3}$	$1\cdot10^{-3}$	$1\cdot10^{-3}$ $3\cdot10^{-3}$
Th 4022,09 3421,19	$3\cdot10^{-3}$ $1\cdot10^{-2}$	$2\cdot10^{-3}$ $5\cdot10^{-3}$	$1\cdot10^{-3}$ $5\cdot10^{-3}$
Pb I 2614,18	$5\cdot10^{-4}$	$1\cdot10^{-3}$	$3\cdot10^{-4}$
P I 2535,65	$1\cdot10^{-3}$	$1\cdot10^{-3}$	$3\cdot10^{-3}$
Sn I 3034,12	$2\cdot10^{-3}$	$5\cdot10^{-3}$	$1\cdot10^{-3}$
Bi I 3067,72 I 2897,98	$1\cdot10^{-3}$ $1\cdot10^{-3}$	$1\cdot10^{-3}$ $3\cdot10^{-3}$	$3\cdot10^{-3}$ $1\cdot10^{-2}$
Zn I 3345,02	$2\cdot10^{-3}$	$1\cdot10^{-2}$	$2\cdot10^{-3}$

When spectra of solutions of $CdCl_2$, $CdSO_4$, $Cd(NO_3)_2$ and $Cd(CH_3COO)_2$ were photographed, using a constant cadmium concentration, no changes in the blackening of the lines were observed, whether capillary electrodes or rotating graphite and copper discs were used (Table 1). In the case of a spark discharge between dry films of cadmium salts deposited on the surface of graphite electrodes, there is observed, in contrast to solutions, a clear relation between line intensity and the anion of the salt.

The systematic errors obtained during analysis of solutions with a variable composition can be reduced, by using a discharge between two surfaces which are being continuously supplied with fresh solution and by adding to the solution sufficiently large amounts of the salts of elements with lower ionization potentials than those of the elements to be determined.

5. The Sensitivity and Reproducibility of the Determination of Elements

In order to establish the sensitivity of the detection of elements in solution when capillary electrodes, and also rotating graphite and copper electrodes are used, the spectra of a series of standard solutions with gradually increasing concentrations of the test elements were photographed under identical conditions; each of the standard solutions contained only one of the elements, the latter being used as the chloride wherever possible. The spectrum excitation conditions were kept constant in all cases. For photographing the spectra, the exposure was chosen so that the continuous background had similar values on the spectrograms.

It is clear from Table 2 that the sensitivity of the detection of elements, either graphite rotating discs or capillary electrodes, differs only slightly. Under these conditions the highest sensitivity of detection (1×10^{-6} - 3×10^{-5}%) is achieved on using the spark lines of Ca, Mg, Be, Zr, Sr, Mo, Ti, and Mn and the resonance arc lines of Cu and Ag. The sensitivity of the detection of the remaining elements given in Table 1, on the basis of their spark and arc lines, amounts to 5×10^{-5} - 1×10^{-2}%.

When copper rotating electrodes are used, the sensitivity ot detection of the elements is the same or somewhat less.

When solutions are analyzed, the sensitivity of the determination of most elements increases by one to two orders, compared with analysis of materials in the solid state.

In order to establish the reproducibility of the spark determination of elements using rotating graphite and copper electrodes, and also capillary graphite electrodes, solutions containing varying amounts of the chlorides of manganese and nickel were analyzed several times; the internal standard used was 0.005% iron in the form of its chloride; titanium was used as the internal standard during the determinations of the concentration of beryllium, boron, and molybdenum. For the determination of the elements indicated, pairs of analytical lines were used which were very close to each other and strongly differed from each other with respect to the excitation conditions; the wave lengths of the lines, whether they belong to the neutral or ionized atoms, and also the values of the excitation potentials of the lines are given in Table 3.

Calibration curves relating the difference in blackening of the analytical lines to the concentration of the test elements (nickel, manganese) are given in Fig. 23; the blackening of the analytical lines is located in the linear section of the characteristic curve of the photographic plate.

The values of the probable error of one determination of nickel and manganese, as found by treating 30 photographs of the spectra are given in Table 3. The errors of a single determination, when using both rotating electrodes and capillary electrodes, depend on the homology of the chosen pairs of lines. When working with sufficiently homologous pairs of lines, the probable error of a single determination amounted to ±4.4-5.3% when rotating discs were used, and ±3-4% when working with capillary graphite electrodes; when nonhomologous analytical pairs of lines, composed of arc and spark lines, were used, the experimental error increased to ±5-11% on using rotating electrodes, and to ±5-14% on using capillary electrodes.

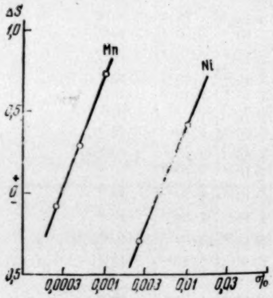

Fig. 23. The relation of the difference in the blackening of the lines Mn 2576.1 and Fe II 2585.9 on the one hand, and of the lines Ni I 3050.8 and Fe I 3020.6 on the other, to the concentration of manganese and nickel in solution.

In order to establish the experimental error which can be attributed to the nonhomogeneity of the photographic emulsion, the measurement of the blackening of the lines, and the conversion from line blackening to intensity, the relative intensity of the homologous spark lines of iron Fe II 2598.369 and Fe II 2599.396 was measured several times. Analysis of the results obtained showed that the probable errors in determining nickel, manganese, boron, beryllium, and molybdenum, which are connected with recording the line intensity, amounted to ±2-3% for nickel and manganese, and ±3-4% for boron, beryllium, and molybdenum. This means that it should be possible to increase the reproducibility of the determinations by using sufficiently homologous lines, and using more accurate methods of recording line intensity, e. g., by switching over from photographing the spectra to direct methods of photoelectric measurements of line intensity.

TABLE 3

Reproducibility of the Determination of Elements during the Spark Analysis of Solutions

Test elements	Analytical pairs of lines A	Excitation potentials, ev	Difference in the excitation potentials, ev	Test concentration limit, %	Probable error of a single determination, %		
					rotating graphite electrode	rotating copper electrode	capillary graphite electrode
Nickel	Ni I 3050,82 Fe I 3020,64	4,09 4,11	0,02	$2,5\cdot10^{-3}$—$1\cdot10^{-2}$	± 5,3	± 5,4	± 3,8
	Ni I 3050,82 Fe II 2585,88	4,09 12,65	8,56		±10,9	±11,4	±13,8
Manganese	Mn II 2576,10 Fe II 2585,88	12,239 12,65	0,41	$2,5\cdot10^{-4}$—$1\cdot10^{-3}$	± 4,4	± 5,1	± 3,0
	Mn II 2949,21 Fe I 3020,64	12,799 4,11	8,69		± 5,3	± 6,9	± 8,0
Boron	B I 2497,78 Ti II 2498,95	4,96	—	$3\cdot10^{-4}$—$1,5\cdot10^{-2}$	—	—	± 5,3
Beryllium	Be I 2348,61 Ti II 2350,66	5,28	—	$3\cdot10^{-5}$—$1\cdot10^{-3}$	—	—	± 7,4
Molybdenum	Mo II 2687,99 Ti I 2669,60	— 4,66	—	$6\cdot10^{-2}$—$2,4\cdot10^{-1}$.	—	—	± 5,8

SUMMARY

One of the main reasons why third elements affect the line intensity of test elements during spark spectrographic analysis of solutions is the change in excitation conditions caused by the presence in solution of elements with low ionization potentials. The effect of the elements is not only related to the value of their ionization potential and atomic concentration, but also to the conditions used for introducing the solution into the spark discharge.

In addition to the clearly manifested relation between the line intensity and the ionization potential, and between line intensity and the atomic concentration of third elements, there is also another less obvious and more complicated effect shown by the elements in solution.

The effect of the elements in solution (the effect is a minimum when the spark is formed between two surfaces of the solution which are not punctured by the spark) increases when one switches over to methods of introducing the solution into the spark, in which processes which occur on solid electrodes become manifest.

The line intensity of the spectrum of a solution, up to the moment at which the film is punctured by a spark, decreases with increasing film thickness, and depends on the viscosity and electrical conductivity of the solution, and on the rate at which the film is renewed.

When capillary and rotating electrodes are used in conjunction with sufficiently homologous pairs of lines the reproducibility (probable error) for a single determination amounts to ± 3-5%.

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THE USE OF A PLASMA GENERATOR AS AN EXCITATION SOURCE IN SPECTROGRAPHIC ANALYSIS*

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In recent years, intensive work has been carried out to develop new spectrum excitation sources, which combine as much as possible the advantages of flame excitation, i.e., stability and the high degree of reproducibility of experimental results related to this, and the advantage of the arc method – the high temperature which ensures a high sensitivity for spectrographic determination.

The present article is devoted to a description of the first results we have obtained during a study of the properties and spectral characteristics of a so-called plasma generator, which has been suggested and used in recent years in techniques as an arc burner for treating and cutting supertough alloys [1-4].

In a burner, whose operational principles have been described previously [3], a high-temperature stream of plasma is formed as a result of thermal and electromagnetic compression of the plasma of a dc arc on lowering the electrical conductivity of its surface layer by cooling with water or an inert gas, and the subsequent ejection of the plasma material from the zone of the arc discharge through a ring cathode. Ejection of the plasma from the cylindrical opening in the cathode occurs at a speed which is several times greater than the speed of sound. This gives a high stability to the stream.

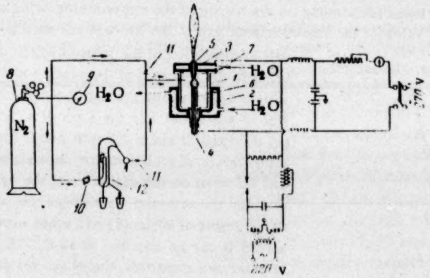

Fig. 1. Schematic diagram of the source. 1) Quartz vessel; 2) cooling jacket; 3) upper lid; 4) graphite rod; 5) cylindrical carbon cathode; 6) carbon anode; 7) asbestos gasket; 8) cylinder of inert gas; 9) manometer; 10) tap; 11) clamp; 12) sprayer.

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* After finishing this work we learned of the results of Margoshes and Scribner (Spectrochimica Acta, 2, 138, 1959); these authors also used a plasma generator for the spectrographic analysis of solutions, and have demonstrated the possibility of using it for the determination of large amounts of iron, chromium, and nickel in steels.

In Fig. 1 is shown a schematic diagram of an experimental plasma generator which we have constructed, together with the electrical circuit of the system, and a diagram of the cooling system. The source consists of a quartz vessel 1, which is placed in a metallic jacket 2 cooled with water, and inside which the electrodes of a dc arc are fitted-anode 6, and cathode 5. The cathode which is fitted into the upper metallic lid 3, also cooled with water, is a carbon tube. Below, through an opening in the bottom of the vessel, is introduced a massive graphite rod 4 onto which the anode is fitted. The shape and dimensions of the electrodes used in these experiments are shown in Fig. 2. The plasma was first cooled with argon, but in subsequent experiments it was cooled with nitrogen gas which was passed into vessel 1, from the cylinder 8 through two symmetrically arranged tubes fused into the side walls of the vessel. The N_2 pressure in the vessel was changed from 0.1 to 0.3 atmosphere and was measured by means of a manometer 9. The main series of experiments, which will form our subject for discussion henceforth, was carried out at an optimum pressure of 0.12-0.14 atm. In order to make sure that only the nitrogen passed out through the cylindrical canal of the cathode, an asbestos gasket was fitted into the gap between the lid 3 and the flange of vessel 1, and the graphite rod of the anode 4 fitted very closely to the walls of the opening into the vessel. For ease of dismantling the source, and also for rapid control during operation of the interelectrode gap, the apparatus was mounted on a spectrographic stand.

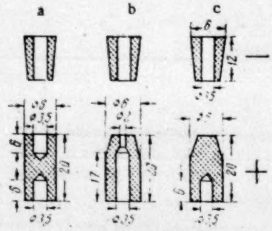

Fig. 2. The form and dimensions of the electrodes: a) For analysis of powders in a source operating under the conditions of a dc arc; b) for analysis of powders in a source operating under the conditions of an impulse arc; c) for the analysis of solutions.

The electrical circuit of the source is similar to that published earlier [5]. It permits work to be carried out with the source under the conditions of an ordinary dc arc, and also under the conditions used for an impulse arc with currents in excess of 30 amp. The construction of the source permits it to be used for the analysis of powders and for studying solutions. In the latter instance, the test sample was introduced into the operating space of the source together with the nitrogen stream by means of the sprayer 12, which is depicted on the lower left part of Fig. 1.

In order to get a stream of plasma, a spark discharge from an IG-2 generator which activated the arc was passed through the interelectrode gap cooled with nitrogen. After an arc discharge had developed (depending on the nature of the experiments being carried out) the spark discharge stopped, while the value of the interelectrode gap in the arc was adjusted to the requisite value. The self-compression of the plasma which occurs as a result of cooling leads to the ejection of the plasma material in the form of a stream, which after passing through the cathode canal appears on the outside of the vessel 1 in the form of a "jet", which has a diameter (at the exit) of about 3.5 mm and is more than 90 mm long. The temperature of such a source depends on a number of factors, first and foremost on the diameter of the cathode opening, the arc current, and the intensity with which the plasma is cooled. According to the result of Weiss [1] and other workers, under appropriate conditions it can be adjusted to 10,000° K and higher. During analysis of powdered materials, the character of the passage of the elements into the plasma of the spectrum-excitation source being studied, depends to a considerable extent on the size of the interelectrode gap. That this is so is evident from a consideration of the curves shown in Figs. 3 and 4. They characterize the change in intensity of the line Ca 3158.9 (Curves 2 and 2') and of the line Si 2514.3 (Curves 1 and 1') with time during evaporation of these elements from a sample of slag in the source operating under the conditions of a dc arc (Fig. 3), and under those of an impulse arc (Fig. 4), for the two extreme values of the interelectrode distances – 3 and 20 mm – used in our experiments. The current was 30 amp. The test

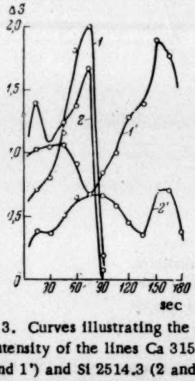

Fig. 3. Curves illustrating the changes in intensity of the lines Ca 3158.9 (1 and 1') and Si 2514.3 (2 and 2') with time, for two values of the interelectrode gap of a dc arc – 3 mm and 20 mm.

sample of slag was placed in the canal of the lower electrode—the anode. In order to get the spectra and to photograph them, the image of the central part of the stream was projected onto the spectrograph slit by means of a one-lens illumination system.*

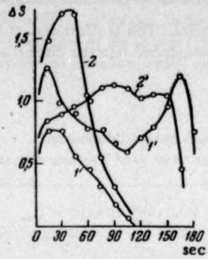

Fig. 4. Curves illustrating the changes in intensity of the lines Ca 3158.9 (1 and 1') and Si 2514.3 (2 and 2') with time, for two values of the interelectrode gap of an impulse arc – 3 mm and 20 mm.

For a small interelectrode distance there is almost no fractionation, and the corresponding curves for changes in the intensity of the analytical lines of various elements with time differ very little from each other, and are characterized by a sharp maximum which appears during the first few dozen seconds of arc burning. With increasing interelectrode distance, fractional distillation of the elements starts to show up more and more clearly. It becomes particularly noticeable when the source is operating under the conditions of a dc arc, and levels down somewhat (as one might expect) on switching over to impulse conditions. The effect of the operating conditions of the source on the character of the passage of the test material into the plasma stream also shows up on the curves reflecting changes in the line intensity of the elements at low interelectrode gaps. While in the case of dc arc conditions there is at first a gradual increase in the rate at which an element passes into the stream, and toward the end there is a sharp increase in this rate, when the conditions of an impulse arc are used, the maximum of the corresponding curves is sharply displaced towards the origin.

The source described is also characterized by the distribution of the atoms and ions of the test material in the plasma stream. In order to study this question, we measured the intensity of the lines of the elements on spectrograms obtained by projecting onto the spectrograph slit various sections of the plasma stream along its length, and also at one section (near the nozzle) across the stream. In Fig. 5 are shown the corresponding results, which illustrate the distribution of the excited atoms and ions of zinc along and across the plasma stream of the source being tested. As is evident, the number of excited atoms in the stream decreases along its length almost linearly. For the ions, toward the end of the stream, a sharper decrease in number is observed, and also a sharper decrease in the intensity of the corresponding lines. In the cross section of the stream, the excited atoms and ions are distributed symmetrically relative to the stream axis according to a "bell-shaped" curve (normal Gaussian distribution).

In order to study the stability of the operation of a plasma generator as a spectrum excitation source (as compared with other sources – a dc arc and an impulse arc), the intensity of the spectral lines of various elements was continuously recorded on a very simple photoelectric setup. The test sample in the form of a powder was placed in the crater of the lower electrode of an arc which was operated either under the conditions used for an ordinary dc arc or under the conditions of an impulse arc. The central part of the plasma stream was projected by means of a condenser system through a light filter onto a photoelement. An ÉPP-09 automatic recorder was used for recording the variations in the photocurrent. In Fig. 6 are compared the curves obtained relating changes in the line intensity of calcium on using an ordinary dc arc, an impulse arc, and a plasma generator as the spectrum excitation source. As is clear from these curves, in contrast to a dc arc and an impulse arc for which there are observed in the plasma of these sources more or less disordered jumps

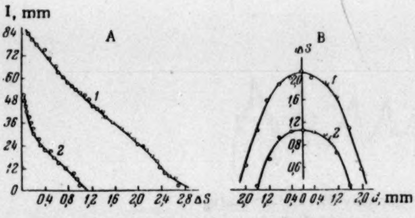

Fig. 5. Change in line intensity of: Zn I 3345.0 (1) and Zn II 2557.9 (2) along (A) and across (B) the plasma stream of the source.

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* The high stability of the stream makes it possible to do without a system for illuminating the spectrograph slit. As an approximate evaluation shows, this increase the intensity of the spectra 5-6 times.

in the line intensity of the element, the line intensity of the element, when the latter is excited in the stream of a plasma generator, proves to be considerably more stable, and the observed variation in the intensity has a much more regular character (externally this appears as the characteristic "breathing" of the plasma stream). An essential factor also is that the degree of stability of a source depends on the distance between the electrodes.

The plasma generator operates even more firmly during the analysis of solutions. This is illustrated in Fig. 7, in which are compared the curves for changes in the line intensity of calcium introduced into the discharge zone of a plasma generator arc in the form of calcium chloride solution, and the curves obtained on analyzing the same solution in an ac arc using a fulgurator [6]. Variations in the intensity of the test element during the operation of this source are very small and are somewhat less than those that one usually meets on using the ordinary methods of analyzing solutions.

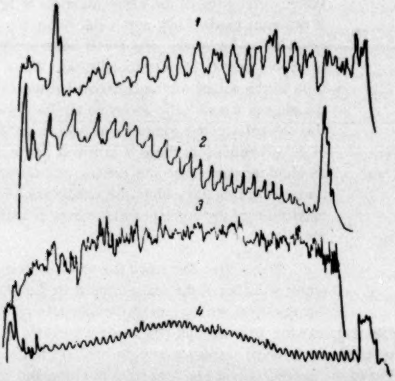

Fig. 6. Variations in the line intensity of calcium during evaporation of the latter from powdered slag in various sources. 1) dc arc; 3) impulse dc arc; 2) and 4) plasma generator operating under the conditions of a dc arc and an impulse arc, respectively.

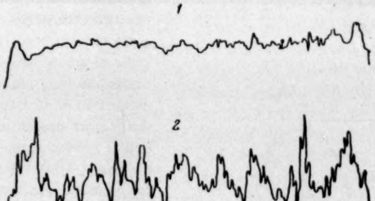

Fig. 7. Variations in the line intensity of calcium during determination of calcium in a solution of $CaCl_2$ by means of a plasma generator (1) and a fulgurator (2).

Turning to the sensitivity of spectrographic determination of the elements by means of the excitation source described – which, by analogy with the flame photometer might conveniently, in our opinion, be called a plasma photometer – then, we conclude, all other conditions being equal, it is somewhat lower than the sensitivity attained by using a dc arc. However, the low value of the background on the spectrograms from the plasma stream, and the possibility of working without using a system for illuminating the spectrograph slit, would, presumably, allow one in the future to increase the sensitivity of a determination. At the same time the high temperature of the source (about 10,000° K) would make such a source convenient for the determination of a number of elements which are difficult to excite under normal conditions.

SUMMARY

The possibility and expediency of using a plasma generator as a source of spectrum excitation in spectrographic analysis have been demonstrated, and a description is given of one of the possible designs of such a source.

The plasma generator differs from other sources by the high stability of its operation, and can ensure high reproducibility of the results of quantitative determination of a large number of elements.

By means of such a high-temperature source one can carry out the analysis of solid powdered materials and of solutions; for the analysis of solutions one can expect particularly high experimental accuracy, comparable with the experimental accuracy obtained on a flame photometer.

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ON SOME ANOMALOUS FORMS OF POLARIZATION CURVES ON A DROPPING MERCURY ELECTRODE

N. V. Nikolaeva-Fedorovich and Yu. M. Povarov

During studies of various electrical reduction reactions on a dropping mercury electrode , one often gets indications of some polarization curves with unusual forms. Some authors in noting this phenomenon, explain the distortion in the shape of the curve by polarographic maxima, although neither the potential region where the "maxima" are observed, nor the relation between the concentration and the nature of the supporting electrolyte indicates that one is dealing with the normal polarographic maxima here. During the polarographic determination of rhenium, Lingane [1], and Geyer [2], for example, observed complex polarograms with maxima which did not disappear on adding organic materials which normally supress maxima of the first and second order quite efficiently. As Geyer points out, of all the materials tested by them, the maximum only disappeared on adding potassium iodide [2]. Distortion of the limiting current wave during reduction of ReO_4^- has also been observed by other authors [3].

Other authors do not give any explanation for the unusual forms of some polarograms, and only indicate that it is impossible to determine various materials polarographically. Unusual forms of polarograms have been obtained during a study of the reduction of niobium on a dropping mercury electrode [4], during the reduction of nickel and cobalt in a supporting electrolyte of potassium thiocyanate [5]. A sharp decrease in the limiting current in a certainpotential range was observed by Filipovic et al.[6] during the reduction of V^V in various buffered solutions, by Bulovová [7] while studying the reduction of indium in a supporting electrolyte of solutions with anions which can be deformed and which are not deformed, and by Souchay [8], and Jenšovkský [9] who studied the conditions for the polarographic determination of IO_4^-. Filipovic and Bulovová are of the opinion that the current drop on the I-φ curve is possibly connected with the reduction of complex anions formed in solution.

As is evident even from this incomplete list of articles, in which there are indications of distortions of the I-φ curves which apparently are not connected with polarographic maxima, polarization curves with unusual shapes crop up often.

In our opinion, the observed distortion of the shape of I-φ curves, or the appearance of maxima which disappear on adding potassium iodide, can be explained in a number of instances by the fact that during the polarographic determination of some materials in a supporting electrolyte of an indifferent electrolyte at a concentration of 1 N and more, formation of complex anions is possible, these anions being then reduced on the dropping mercury electrode; the present authors relate the polarization curves thereby obtained, however, not to the reduction of the anions formed in solution, but to the reduction of the original materials taken for analysis.

A consideration of the experimental results given in the articles mentioned above confirms this explanation: the sharp drops in the current on the polarization curves for the reduction of rhenium, indium, etc., are observed at potentials approximating to the potential for the zero discharge of mercury, when there occurs a shift from a positively charged surface of the mercury to a negatively charged surface. At present, on the basis of a large amount of experimental data, it has been shown that the current drops observed in the region of negative charges on the electrode surface are characteristic for electrical reduction of at least two and more charged anions. The first current drop in I-φ curves was observed by Kryukova during the reduction of $S_2O_8^{2-}$ on a dropping mercury electrode [10]. Subsequently, the slowing down of the reduction of anions was noted in a number of articles during the reduction of other anions [11].

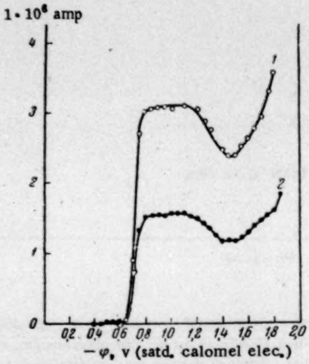

Fig. 1. $K_2Ni(SCN)_4$ in a solution of 1 N KSCN. Concentration of the complex: 1) 2×10^{-3} N; 2) 1×10^{-3} N.

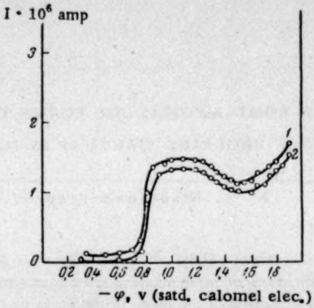

Fig. 2. 10^{-3} N $K_2Ni(SCN)_4$ in a solution of 1 N KSCN: Curves taken: 1) after 1 hour; 2) after 2 hours.

The phenomenon of the current drop was explained by electrostatic repulsion of the negatively charged anions by the negatively charged electrode surface, which leads to a drop in the concentration of the anions in the surface layer. On addition of an indifferent electrolyte, the drop in current during reduction of certain anions disappears. This could be explained by the fact that on increasing the concentrations of the cations of the supporting electrolyte, the electrical field of the negative charges of the electrode decreases. In some cases, on the other hand, addition of an indifferent electrolyte merely limits the region over which there is a drop in current, while the reaction is still slowed down.

As an example substantiating the explanations given above for the distortion of the polarization curves, we would like to give the experimental results we have obtained during the reduction of the thiocyanate complexes of nickel and cobalt on a dropping mercury electrode.

As pointed out already, polarographic curves of unusual shape which have been obtained during the reduction of Ni^{2+} in a supporting electrolyte of KSCN have been given in cetain articles [5]. These distortions of the I-φ curves could be explained on the grounds that, during the polarographic determination of nickel and cobalt in a supporting electrolyte of KSCN, reduction occurs, not of the cations Ni^{2+} and Co^{2+}, but of the complex anions of these metals which are formed in the electrolyte in the presence of KSCN, and during the reduction of which, there may be observed drops in the current in the area of the limiting current. In order to exclude the effect of other anions, we synthesized the complexes $K_2Ni(SCN)_4$ and $K_2Co(SCN)_4$, and studied their reduction on a dropping mercury electrode. All the potential values are quoted with respect to a saturated calomel electrode.

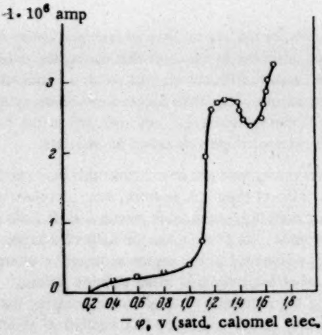

Fig. 3. 2×10^{-3} N $K_2Co(SCN)_4$ in a solution of 1 N KSCN.

In Fig. 1 are given the polarization curves for the reduction of $K_2Ni(SCN)_4$ in a supporting electrolyte of 1 N KSCN. Reduction starts at $\varphi = -0.70$ v; the current increases and reaches the value of the limiting current. At $\varphi = -1.2$ v, there is observed a current drop, and, after reaching some minimum current value, the reaction rate increases. In the region of the limiting current there is observed a proportionality between the values of I_d and the concentration of the complex. The polarization curves for the reduction of $K_2Ni(SCN)_4$ in a supporting electrolyte of KSCN change with time, although the current drop does not disappear even after the solution has been allowed to stand for a long time in the cell (Fig. 2). A decrease in the concentration of KSCN leads to the disappearance of the wave, which is connected with the dissociation of the complex in the presence of low concentrations of potassium thiocyanate [12, 13].

The polarization curves for the reduction of $K_2Co(SCN)_4$ are shown in Fig. 3. In a supporting electrolyte of 1 N KSCN reduction of the complex starts at a potential of $\varphi = -1.15$ v. The value of the limiting current is proportional to the concentration of the complex. At a potential of $\varphi = -1.4$ v, the current starts to drop, and again increases at potentials which are more negative than $\varphi = -1.5$ v. The current drop in the case of the reduction of $K_2Co(SCN)_4$ is not so clearly marked as in the case of the reduction of $K_2Ni(SCN)_4$. By comparing the I-φ curves for the reduction of these complexes, it is possible to understand why the diffusion current of cobalt is very unstable during the determination of cobalt in the presence of nickel in a supporting electrolyte of potassium thiocyanate [5]; reduction of $K_2Co(SCN)_4$ in a supporting electrolyte of 1 N KSCN starts at a potential of $\varphi = -0.15$ v, while the current drop on the reduction curve for 10^{-3} N $K_2Ni(SCN)_4$ + 1 N KSCN starts at $\varphi = -1.2$ volt, which is the reason for the instability of the limiting current for the reduction of cobalt.

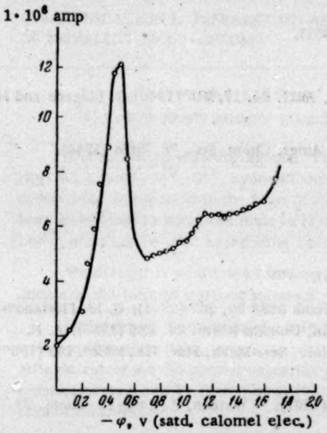

Fig. 4. 4×10^{-3} N $Pt(NH_3)_2(OH)_2Cl_2$.

If one assumes that the sharp current drop in the region of the negative charges on the surface on passing through the potential of the point of zero charge is connected with the reduction of complex anions which are formed in solution, it is possible to explain many phenomena observed by various authors during a study of the reduction of certain materials. Suppression, for example, of the polarographic maximum by potassium iodide during the reduction of ReO_4^- can be explained by the fact that, in a supporting electrolyte of 2 N and 4 N HCl, it is not a polarographic maximum that is observed but a polarization curve for the reduction of the complex anion, possibly of $ReCl_6^{2-}$ [1, 14] on which there is a current drop in the region of the potential of zero charge. Addition of the iodide anion suppresses the reduction of the anions when there are positive charges on the electrode surface [2, 3], and the reduction potential of the complex anion shifts toward more negative potentials at which there is observed an increase in the current after the minimum.

Having mistakenly taken the increase in the reduction current of the anion, with its subsequent drop during overcharging of the electrode surface, for a polarographic maximum, the authors naturally could not explain why the maximum disappeared only on adding KI. It is impossible, of course, to affirm that unusual forms of the polarization curves which are observed during polarographic determinations are always connected with reductions of anions; however, we should like to bring attention to the possibility that this may be so. The form of the polarographic curves can also change as a result of exchange reactions between the complex anions and the anions of the supporting electrolyte [15].

The slowing down of electrical reduction reactions when the electrode surface is negatively charged is observed not only in the case of the reduction of complex anions, but also, as Kivalo and Laitinen [16] discovered recently, in the case of the reduction of neutral particles, for example, cis-$Pt(NH_3)_2Cl_2$. We have also observed a current drop during the reduction of the neutral complex $PT(NH_3)_2(OH)_2Cl_2$ (Fig. 4).

This phenomenon can be explained by the reduction of the complex anions which are formed during the hydrolysis of the original salt, or by the fact that although the particle as a whole is not charged, the atoms of chlorine which form part of it carry negative charges, and adsorption of these on the electrode surface becomes more difficult as the negative charge increases [17].

SUMMARY

The polarographic reduction of the thiocyanate complexes of nickel and cobalt have been studied on a dropping mercury electrode. It has been shown that the distortion of the polarographic curves which is observed in a number of cases can be explained by reduction of complex anions which are formed in solution.

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MOLYBDENOMETRY

COMMUNICATION I. PREPARATION AND STANDARDIZATION OF SOLUTIONS OF TRIVALENT MOLYBDENUM

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The following reducing agents: Ti^{III}, Cr^{II}, Fe^{II}, Sn^{II}, As^{III}, Cu^{I}, V^{II}, $Fe(CN)_6^{4-}$, SO_3^{2-}, $S_2O_3^{2-}$, I^-, H_2O_2, $Hg_2(NO_3)_2$, Mo^V, W^V, U^{IV}, hydroquinone, ascorbic acid, hydrazine, and some other compounds have found more or less wide application in the form of standard solutions in analytical chemistry. The appropriate methods have been considered in numerous reviews [1-6]. Compounds of a number of other elements of lower valence (Nb^{III}, Mo^{III}, etc.) can be used as reducing agents.

We thought it would be of interest to make a systematic study of the possibility of using trivalent molybdenum in the form of standard solutions for determining various elements, in particular sexivalent molybdenum.

Molybdenum forms compounds in which it is found in the sexi-, quinque-, and trivalent state. Moreover, under certain conditions, complex compounds are formed in which molybdenum exhibits a valence of four. No reliable values for the normal oxidation potentials of Mo^{VI}/Mo^V and Mo^V/Mo^{III} are available. Results of measurements made by Förster et al [7], and, particularly results obtained by Höltje and Geyer [8], give some idea of these values.

Redox Potential of Molybdenum in 5 N HCl [8] (Temperature 20°, platinum electrode)

Total Mo concentration, mole/liter	0,250	0,125	0,083	0,050	0,035
Mo (VI/V) (1 : 1), v	+0,53	+0,53	+0,53	+0,54	+0,54
Mo (V/III) (1 : 1), v	+0,14	+0,17	+0,19	+0,20	+0,21

Available results show that solutions of trivalent molybdenum salts possess fairly strong reducing properties and deserve systematic study as titrants for the determination of sexivalent molybdenum and other elements in their higher valence states (Fe^{III}, Mn^{VII}, Cr^{VI}, V^V, Cu^{II}, Se^{IV}, Te^{IV}), and also for the determination of some organic materials.

No potential jumps corresponding to the reduction of molybdenum to the quadrivalent state are observed on the potentiometric titration curves of sexivalent molybdenum in a medium of hydrochloric or sulfuric acid with solutions of such strong reducing agents as divalent chromium salts, even when the most diverse conditions are used. Upon observing titration curves of solutions of trivalent molybdenum with permanganate, dichromate, and other oxidizing agents, one notes, depending on the conditions used, a potential jump corresponding to completion of conversion of molybdenum to the quinquevalent or sexivalent state. Thus, it may be assumed that during titration with a solution of trivalent molybdenum, the latter will change into the quinquevalent state, and, subsequently, in the case of strong oxidizing agents, to the sexivalent state.

Gapchenko [9] has used trivalent molybdenum solutions as a reducing agent for the titrimetric determination of picric acid, cupferron, iron, and cobalt.

PREPARATION AND STORAGE OF TRIVALENT MOLYBDENUM SOLUTIONS

Reduction of sexivalent molybdenum to the trivalent state has been studied several times, mainly in connection with its quantitative determination by titrimetric methods. A review of such work can be found in Gmelin's textbook [10], and also in the article by Höltje and Geyer [8]. Methods of preparing some trivalent molybdenum compounds have also been described in the article of Hartmann and Schmidt [11], which is devoted to a study of the complex compounds of trivalent molybdenum. The most promising methods for preparing trivalent molybdenum solutions are those based on reduction by means of amalgamated zinc and reduction on a lead cathode.

The simplest method of preparing standard solutions of trivalent molybdenum is the reduction of acid solutions of ammonium molybdate by means of amalgamated zinc. However, the trivalent molybdenum solutions prepared in this way will contain zinc ions, which in certain cases may interfere during titration.

Preparation of trivalent molybdenum solutions by electrical reduction requires relatively more complicated apparatus; the advantage of this method is that the solutions obtained are free from foreign ions.

a) Preparation of Trivalent Molybdenum Solutions by Reduction of Sexivalent Molybdenum with Amalgamated Zinc.

The apparatus used for preparing and storing a solution of trivalent molybdenum is shown in Fig. 1.

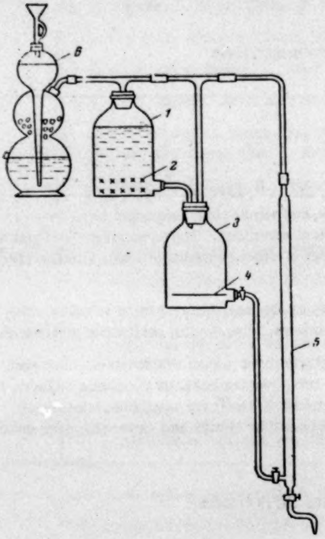

Fig. 1. Apparatus for preparing and storing trivalent molybdenum solutions: 1) 2-3 liter bottle for preparing molybdenum; 2) granulated amalgamated zinc; 3) 2-3 liter bottle for storing trivalent molybdenum solution prepared in bottle 1; 4) concentrated hydrochloric acid or KCl; 5) 25 or 50 ml buret; 6) Kipp apparatus for preparing carbon dioxide.

Preparation of a Hydrochloric Acid Solution of Trivalent. Molybdenum. In order to prepare 2 liters of 0.05 M trivalent molybdenum, 17.7 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ is dissolved in 2 liters of 2 N HCl. The solutions obtained is transferred to bottle 1, which contains 500 g of amalgamated zinc. The bottle is closed with a stopper fitted with tubes (see Fig. 1), which connect with the buret of the bottle in which the solution is to be stored, and to a Kipp apparatus used for generating CO_2. Bottle 3 contains concentrated hydrochloric acid or crystalline potassium chloride (100 g per liter of final solution). After 10-15 minutes the color of the molybdate solution in bottle 1 changes from red-brown to green, and after 1.5-2 hours a dark-green solution of trivalent molybdenum is obtained; the latter is transferred to bottle 3 for storage; concentrated HCl or KCl increase the stability of trivalent molybdenum solutions.

The hydrogen which is liberated during the reduction of sexivalent molybdenum in bottle 1, should be allowed to issue outward through the Kipps apparatus; for this purpose the tap should be left open all the time. It should be noted that during the reduction of sexivalent molybdenum with amalgamated zinc in a hydrochloric acid medium; a large amount of hydrogen is liberated which passes out through the buret as well. When reduction is complete, the buret tap is closed.

In order to establish the extent to which the sexivalent molybdenum has been reduced to the trivalent state, the concentration of trivalent molybdenum is first determined by potentiometric titration with molybdate, dichromate, or cupric sulfate. The total molybdenum is then determined by potentiometric titration of the sexivalent molybdenum by means of solutions of Mo^{III} or $CrCl_2$ after oxidation of Mo^{III} and Mo^{V} with permanganate, the excess of which is reduced by addition of Na_2SO_3 until the solution has been decolorized.

In this way it was established that under the experimental conditions used, 85-90% of the sexivalent molybdenum was reduced to the trivalent state. The rest of the molybdenum was in the quinquevalent state.

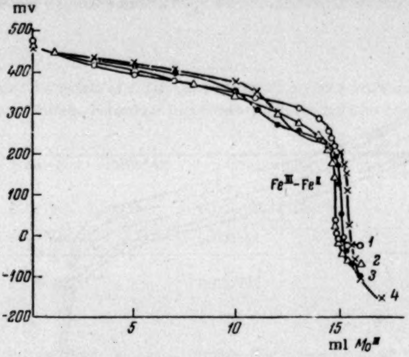

Fig. 2. Titration curves for trivalent iron in a sulfuric acid medium: 10.0 ml of 0.1000 N $K_2Cr_2O_7$, 0.6 g of Mohr's salt and sulfuric acid taken; $T_{Mo^{III}/Mo^{IV}} = 0.006483$; Room temperature; Titration vessel 150 ml capacity. 1) 40 ml H_2SO_4 1:1, 10 ml concentrated H_2SO_4; 2) 40 ml H_2SO_4 1:1; 3) 40 ml H_2SO_4 1:2; 4) 40 ml H_2SO_4 1:5. The potential jumps on the platinum electrode occur on addition of 14.9, 15.1, and 15.5 ml of trivalent molybdenum solution.

Preparation of a Sulfuric Acid Solution of Trivalent Molybdenum. In order to prepare 0.05 M trivalent molybdenum solution, 8 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ is dissolved in 900 ml of 4 N H_2SO_4 and the solution obtained reduced with amalgamated zinc in the bottle of the apparatus. Reduction of sexivalent molybdenum to the trivalent state proceeds more slowly in this case than when hydrochloric acid is used. Strongly amalgamated zinc reduces molybdenum slowly in a H_2SO_4 medium. Reduction is still incomplete even after one month. In all cases the sexivalent molybdenum is not reduced to the trivalent state by more than 70%. It should be noted that the sulfuric acid solution of trivalent molybdenum appreciably attacks rubber and is unstable in air. Accordingly, a sulfuric acid solution of trivalent molybdenum cannot be recommended for wide application in practice as a reducing agent.

b) Preparation of Trivalent Molybdenum Solutions by Reduction of Sexivalent Molybdenum on a Lead Cathode.

Hydrochloric solutions of Mo^{III} are obtained by electrolytic reduction of MoO_3 solutions as follows [12].

A solution of 20 g of MoO_3 in 150 ml concentrated HCl is diluted to 200 ml and is reduced with a diaphragm on a lead cathode at a current density of 1-2 amp/cm^2. The anode liquid is 15% HCl. An amalgamated lead cathode can also be used for preparative purposes. The cathode is amalgamated after each electrolysis [13].

The solution obtained is diluted to the requisite concentration and then standardized.

In some cases it is more convenient to isolate trivalent molybdenum in the form of crystalline K_3MoCl_6 [12, 14] or $(NH_4)_3MoCl_6$ [14]. These compounds are completely stable in air and can be prepared beforehand in large amounts. A solution of MoO_3 (35 g) in 8 N HCl (350 ml) is electrolytically reduced to Mo^{III}; the solution is evaporated to 150 ml (33% $MoCl_3$) and is then saturated with HCl, one half or three quarters of the calculated amount of KCl is added (30-40 g) in the form of a 10% aqueous solution, and the solution evaporated at 70° under reduced pressure until crystals start to separate out; the filtrate is saturated with HCl while the solution is cooled, and the compound which separates out washed successively with concentrated HCl, alcoholic HCl, and alcohol, and finally dried under vacuum. Brick-red crystals of K_3MoCl_6 are thus obtained.

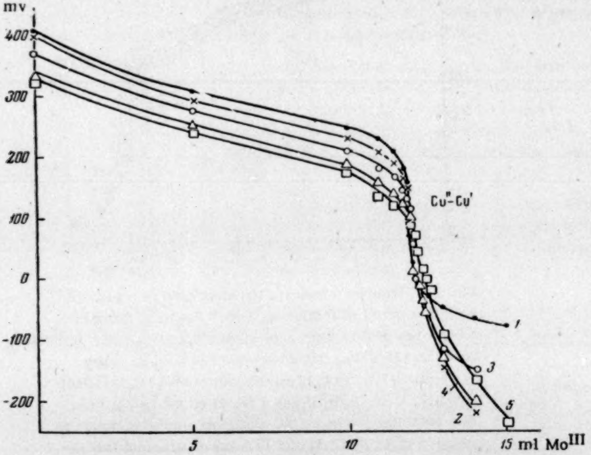

Fig. 3. Curves obtained during the titration of divalent copper with trivalent molybdenum solution in a hydrochloric acid medium: 10.0 ml of 0.1000 N $CuSO_4 \cdot 5H_2O$ and 60 ml of hydrochloric acid of varying concentration taken; room temperature; $T_{Mo^{III}/Mo^{V}} = 0.007996$; capacity of titration vessel 150 ml. 1) HCl 1:1; 2) HCl 1:2; 3) HCl 1:3; 4) HCl 1:4; 5) HCl 1:5. The potential jump of the platinum electrode occurred on addition of 12.00; 12.04; 12.10; 12.15 and 12.20 ml of Mo solution respectively.

In order to prepare $(NH_4)_3MoCl_6$, 20 g of chemically pure ammonium molybdate is dissolved in 150 ml of concentrated hydrochloric acid and the solution diluted to 200 ml with water; this solution is then electrolyzed at a current density of 1-2 amp/cm^2 on a lead cathode for2-3 hours. The anode liquid is 1:1 HCl. During this process the color of the solution changes from a weak yellow to brown. Next, 50 ml of a saturated NH_4Cl solution is added. After this, gaseous HCl is passed through the solution for 20-30 minutes. The brown precipitate of $(NH_4)MoCl_6$ which separates out is filtered off and is dried in air.

The potassium and ammonium salt are equally suitable for preparing standard solutions of trivalent molybdenum. An amount of 18.2 g of $(NH_4)_3MoCl_6$ is dissolved in 1 liter of 3 N hydrochloric or sulfuric acid (saturated with CO_2) in a bottle with a capacity of 2 liters, which is sealed with a stopper containing tubes leading to a buret and to a Kipp apparatus with marble and hydrochloric acid. The solution obtained is red-brown.

STANDARDIZATION OF TRIVALENT MOLYBDENUM SOLUTION

The trivalent molybdenum solution was standarized potentiometrically by means of potassium dichromate, cupric sulfate, and molybdate.

Standardization of the Trivalent Molybdenum Solution by means of Potassium Dichromate. In order to standardize a trivalent molybdenum solution, a 0.1000 N solution of $K_2Cr_2O_7$ was prepared by dissolving the exact amount of the chemically pure salt in 1 N sulfuric acid in a standard flask. An amount of 10.0 ml or 20.0 ml of the dichromate solution was pipetted into the titration vessel, and 40 ml of sulfuric acid 1 : 1 and 10 ml of concentrated sulfuric acid added; CO_2 was passed through the solution for 15 minutes and then 0.6 or 1.2 g of Mohr's salt free from trivalent iron added; the carbon dioxide was bubbled through the solution for a further 5-10 minutes, and then the trivalent iron formed titrated at room temperature with the trivalent molybdenum solution until a potential jump was obtained. The change in potential of a platinum electrode during tritration of trivalent iron is shown in Fig. 2. This method gives accurate and readily reproducible results. The reactions which occur can be expressed by the following equations:

TABLE 1

Comparison of the Factor of a Trivalent Molybdenum Solution Standardized against Cupric Sulfate, Potassium Dichromate, and Ammonium Molybdate

Solution No.	By ammonium molybdate	By cupric sulfate	By potassium dichromate
1	0,007992; 0,008000	0,008008; 0,008008; 0,007968	0,007988
2	0,002466	0,002460	—
3	0,006454	—	0,006448 0,006448
4	0,007986	0,007982	0,007988

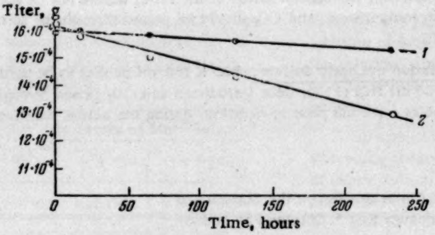

Fig. 4. Stability of trivalent molybdenum solutions during storage; 1) Solution prepared by dissolving $(NH_4)_3MoCl_6$ in hydrochloric acid; 2) solution prepared by dissolving $(NH_4)_3MoCl_6$ in sulfuric acid.

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ = 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

$$2Fe^{3+} + Mo^{III} = 2Fe^{2+} + Mo^{V}.$$

Direct titration of potassium dichromate with a trivalent molybdenum solution gives less reliable results.

During a study of the effect of the sulfuric acid concentration in the solution being titrated on the accuracy of the standardization of the trivalent molybdenum solution by means of potassium dichromate, it was established that the lower the sulfuric acid concentration in the solution being titrated, the later the titration end point corresponding to completion of reduction of Fe^{III} to Fe^{II} (Fig. 2) will occur. The potential jump at the endpoint is greater, the higher the sulfuric acid concentration. Reduction in a medium of concentrated sulfuric acid (above 18 N H_2SO_4) proceeds fairly rapidly, while in a medium of dilute sulfuric acid it is very slow, and in order to get a stable electrode potential, it is necessary to wait 3-4 minutes near the endpoint.

For removing oxygen dissolved in the solution being titrated it is sufficient to pass CO_2 through it for 15-20 minutes at the rate of 3-4 bubbles a second.

In order to study the effect of temperature on standardization of trivalent molybdenum by means of potassium dichromate, 10 ml of 0.1 N potassium dichromate, 40 ml of H_2SO_4 (1 : 1), 10 ml of concentrated H_2SO_4, and 0.6 g of Mohr's salt were introduced into a 150 ml beaker; CO_2 was passed through the solution for 20 minutes at the rate of 3-4 bubbles a second.

TABLE 2

Changes in the Factor of a Trivalent Molybdenum Solution in the Presence, and the Absence of Amalgamated Zinc (10 ml of 0.09950 N potassium dichromate taken for each titration)

In the presence of amalgamated zinc			In the absence of amalgamated zinc		
time, hr	amount of Mo^{III} used for the titration, ml	$T_{Mo^{III}/Mo^{VI}}$	time, hr	amount of Mo^{III} used for the titration, ml	$T_{Mo^{III}/Mo^{IV}}$
0	11,05	0,008640	0	11,72	0,008145
23	11,58	0,008245	14	11,74	0,008132
33	11,88	0,008037	24	11,75	0,008125
80	13,59	0,007026	38	11,78	0,008104
99	15,05	0,006343	89	12,21	0,007820
141	17,85	0,005348	145	12,46	0,007663

It was found that the titration endpoint occurs considerably earlier at 80-90°, while the value of the potential jump at the endpoint is considerably smaller than that at room temperature. However, at room temperature the endpoint corresponds accurately to the equivalence point. The factor found under such conditions for the Mo^{III} solution when dichromate was used agrees with the factor found by the molybdate method ($T_{Mo^{III}/Mo^{III-V}}$ = = 0.003645 by the molybdate method, $T_{Mo^{III}/Mo^{III-V}}$ = 0.003653 by the dichromate method).

On the basis of the results obtained, it may be concluded that in order to standardize trivalent molybdenum by means of potassium dichromate in a sulfuric acid medium, the concentration of the latter should not be less than 18 N, while the titration should be carried out at room temperature, and CO_2 should be passed through the solution for 20-25 minutes prior to titration.

Standardization of Molybdenum Trichloride Solution by Cupric Sulfate. Into a 150-ml beaker to be used for titration, 10.0 ml of 0.1000 N cupric sulfate and 60 ml HCl (1:1), were introduced and CO_2 passed through the solutions for 25-30 minutes at the rate of 3-4 bubbles a second prior to titration; during the actual titration,

TABLE 3

The Effect of Hydrochloric Acid Concentration on the Stability of the Factor of a Trivalent Molybdenum Salt * Obtained by Reduction with Amalgamated Zinc

Conc. HCl added per liter Mo^{III} sol, ml / Days	50	200	250	300
0	0,007334	0,007075	0,006410	0,008148
3	0,007288	0,006979	—	—
4	—	—	0,006410	—
6	0,007240	0,006950	—	0,008442
7	—	—	0,006393	—
8	0,007180	—	—	—
10	—	—	—	0,008142
11	—	—	0,006368	—
14	—	—	0,006351	—

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* Hydrochloric acid concentration in the original solution obtained was 2 mole/liter.

the rate at which CO_2 was passed through the solution was approximately doubled; the solution was finally titrated with the Mo^{III} solution at room temperature. During this procedure, Cu^{2+} ions are reduced stepwise according to the following scheme:

$$2CuCl_4^{2-} + Mo^{III} \rightarrow 2CuCl_2^- + Mo^V$$

$$2\,CuCl_2^- + Mo^{III} \rightarrow 2Cu^0 + Mo^V .$$

When the first reaction was complete, a distinct potential jump was observed at the equivalence point. When the second reaction was complete no potential jump was observed at the titration endpoint. In order to calculate the factor of the trivalent molybdenum solution, the titration results obtained for the first reaction were used. The change in the potential of the platinum electrode during titration of copper is shown in Fig. 3.

When atmospheric oxygen is present in the solution being titrated, the $CuCl_2^-$ ions formed in the titration vessel are oxidized, as is the solution of Mo^{III} issuing from the buret. Accordingly, the tip of the buret was immersed in the solution which was being titrated, while a layer of benzene was placed above the latter. In order to remove oxygen dissolved in the solution being titrated, it was sufficient to pass CO_2 through it for 30 minutes at the rate of 2-3 bubbles a second.

Despite passing CO_2 through the solution to be titrated at the rate of 2-3 bubbles a second, somewhat more of the Mo^{III} solution was used up than was necessary for reducing Cu^{2+} to Cu^I. This can be explained by the fact that small amounts of oxygen remaining in the titration vessel oxidize $CuCl_2^-$ and Mo^{III}.

Although the effect of atmospheric oxygen can be prevented by placing a layer of benzene on top of the solution to be titrated, the use of benzene complicates the method, and it is not economical. Accordingly, we tried to eliminate interference from oxygen in the titration vessel without resorting to the use of benzene. In order to do this the following technique was adopted. A large part of the Mo^{III} solution was added from the buret, the tip of which was immersed in the solution being titrated. Near the titration endpoint the buret tip was placed above the solution so as to follow the dropwise addition of Mo^{III} solution. During this procedure the CO_2 rate through the solution being titrated was increased to 4-5 bubbles a second. When such conditions were used, satisfactory results were obtained without using benzene.

TABLE 4

The Stability of the Factor of Trivalent Molybdenum Solution on Storage (obtained by dissolving $(NH_4)_3MoCl_6$

Time, hr	Factor of Mo^{III} sol.	
	3 *N* HCl	3 *N* H_2SO_4
0	0,001594	0,001623
17	0,001592	0,001577
65	0,001579	0,001499
125	0,001556	0,001424
234	0,001521	0,001289

In order to establish the effect of the acid concentration of the solution being titrated on the standardization of the Mo^{III} solution by means of cupric sulfate, 10.0 ml of 0.1000 N $CuSO_4 \cdot 5H_2O$ was introduced into a 150 ml titration vessel, and 60 ml of hydrochloric acid (1:1, 1:2, 1:3, 1:4, and 1:5) was added; CO_2 was then bubbled through the solution to be titrated for 30 minutes at the rate of 3-4 bubbles a second; during the titration the CO_2 rate was increased to 4-5 bubbles a second. Titration was carried out at room temperature.

The results obtained (Fig. 3) show that with decreasing hydrochloric acid concentration of the solution being titrated, the titration endpoint occurs later than the equivalence point corresponding to the completion of the reduction of Cu^{II} to Cu^I. In addition, the potential jump decreases with decreasing acid concentration. Reduction of the copper proceeds fairly rapidly.

On the basis of the results obtained, it can be concluded that Mo^{III} solutions can be standardized against cupric sulfate in a HCl medium 1:1 (volume of solution 60 ml) under conditions such that CO_2 is passed through the solution at the rate of 3-4 bubbles a second for 25-30 minutes prior to titration, while the CO_2 rate is increased to 4-5 bubbles a second during the actual titration. This method also gives accurate and readily reproducible results.

Standardization of Trivalent Molybdenum Solutions by Means of Ammonium Molybdate. The factor of a trivalent molybdenum solution can be checked by potentiometric titration of ammonium molybdate:

$$2\,MoO_4^{2-} + Mo^{III} + 16H^+ = 3\,Mo^V + 8\,H_2O.$$

The molybdenum content of the solution was determined gravimetrically as lead molybdate. Conditions for the titration of sexivalent molybdenum will be described in a future communication.

As Table 1 shows, almost identical results are obtained when a trivalent molybdenum solution is standardized either against potassium dichromate, cupric sulfate, or ammonium molybdate.

Potassium bromate and potassium iodate are not suitable as original materials for standardizing Mo^{III} solutions, since during titration trivalent molybdenum is oxidized by a solution of potassium bromate and iodate, not only to the quinquevalent state, but also to the sexivalent state, and in addition the quinquevalent molybdenum, which is usually present in the trivalent molybdenum solution, is also oxidized. This leads to incorrect results. Potassium bromate and potassium iodate can only be used for standardizing trivalent molybdenum solutions as long as the latter are free from quinquevalent molybdenum.

STABILITY OF THE FACTOR OF SOLUTIONS OF TRIVALENT MOLYBDENUM DURING STORAGE

As is evident from Table 2, a solution of trivalent molybdenum is less stable when stored in the presence of amalgamated zinc than in its absence. This can be explained by the fact that amalgamated zinc in a hydrochloric acid medium interacts with hydrogen ions according to the following equation:

$$Zn + 2H^+ = Zn^{2+} + H_2.$$

Trivalent molybdenum probably lowers the hydrogen overvoltage on the amalgamated zinc. Accordingly the acid concentration gradually decreases. With decreasing acid concentration there is formed a dark-brown precipitate as the result of the hydrolysis of trivalent molybdenum.

From the results given in Table 3, it is clear that the stability of solutions of trivalent molybdenum increase during storage with increasing hydrochloric acid concentration. Potassium chloride has approximately the same effect. When 100 g of potassium chloride is added to 2 liters of Mo^{III} solution in a 2 N HCl medium, the factor of the solution hardly changes at all over a period of 14 days. This effect presumably is connected with a decrease in dissociation of the chloride complexes of trivalent molybdenum, and with an increase in the potential of Mo^V/Mo^{III}.

On the basis of the results obtained it can be regarded as established that a trivalent molybdenum solutions must be separated from amalgamated zinc during storage. Moreover, it is essential to maintain a high chloride concentration in the trivalent molybdenum solution.

The fact that the factor of the solution remains unchanged indicates that reduction of H^+ ions by trivalent molybdenum ($2H^+ + Mo^{III} = H_2 + Mo^V$) hardly occurs at all.

Table 4 contains results which characterize the stability of trivalent molybdenum solutions obtained by dissolving a preparation of $(NH_4)_3MoCl_6$.

Solutions of trivalent molybdenum in hydrochloric acid are considerably more stable than solutions in sulfuric acid (Fig. 4).

Although the factor of trivalent molybdenum solutions hardly changes at all for several days when high concentrations of hydrochloric acid or potassium chloride are used, nevertheless the factor should be checked every two to three days.

SUMMARY

Standard solutions of trivalent molybdenum undoubtedly are of certain importance for analytical chemistry, since they possess strong reducing properties, are comparatively easily prepared by reducing ammonium molybdate with amalgamated zinc or on a lead amalgamated cathode, and are sufficiently stable when they are stored and used under appropriate conditions.

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POLAROGRAPHIC DETERMINATION OF GOLD ON A ROTATING MICRODISC PLATINUM ELECTRODE

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Polarographic determination of gold on a dropping mercury electrode is difficult because of the chemical interaction of many gold compounds with mercury metal. Usually complexing agents are used which form compounds with gold which are stable to mercury metal [1-10].

The behavior of gold toward reduction on solid electrodes has not hitherto been studied in detail, although there are individual references to the possibility of using such electrodes for the polarographic determination of gold [11, 12]. Ezerskaya [6] using a rotating platinum wire electrode, obtained a gold wave which is not clearly defined enough for direct quantitative polarographic determination. This author has, however, successfully titrated gold amperometrically. While investigating the properties of a rotating wire electrode, the back part of which was screened with a ceresin coating, Ferret and Phillips [13], in addition to other metals, determined gold polarographically.

We studied the reduction of gold on a platinum microdisc electrode, and also the possibility of using the latter for the polarographic determination of gold.

A M7-2000 visual polarograph of the Gorky Institute of Chemistry was used in conjunction with a GZS-47 mirror galvanometer which had a maximum sensitivity of 10^{-9} amp/mm.

An electrode (Fig. 1) which could be called a microdisc electrode was used. It was in the form of a platinum wire fused into a glass tube. The bottom part of the tube and the platinum were carefully polished. Contact was established through mercury in which a copper wire was immersed. The surface area of the platinum cathode was 0.78 mm^2.

A platinum plate with an area of 400 mm^2 was used as the anode, as well as an external anode – a saturated calomel element plus mercury with sufficiently large area.

The rotational speed of the electrode was kept constant at 800 rpm. A vessel described previously [14] was used as the electrolyzer.

A standard gold solution was prepared from commercial chloroauric acid. The concentration of the standard solution was determined gravimetrically [15, 16]; it was found to be 0.0103 g/ml. More dilute solutions were prepared by diluting the standard solution.

Experiments showed that in a supporting electrolyte of 0.1 M $NaNO_3$ or KCl from which oxygen had been removed by passing nitrogen through the solution, the gold from the solution of chloroauric acid is reduced on a platinum microdisc rotating electrode, and gives a clear cut polarogram with two diffusion regions (Fig. 2, Curve 3). The first break on the curve, at a potential of + 0.6 v (relative to the saturated calomel electrode) is accompanied by deposition of metallic gold on the electrode, and corresponds to the process $[AuCl_4]^- + 3e \rightarrow Au^0 + 4Cl^-$. The second break on the curve, as in the case of the reduction of chloroplatinic acid [17], corresponds to electrical reduction of hydrogen ions.

Oxygen which is dissolved in water, since it is reduced on a platinum microelectrode, gives a distinct wave and interferes with the determination of many ions. Bearing in mind that gold is reduced at a more positive potential (+0.6 v with respect to the saturated calomel electrode) than oxygen (+0.2 v) it should be possible to omit the removal of oxygen which is necessary in other cases [14, 17]. It is clear from Fig. 2 that in the given test solution, oxygen does not affect the gold wave.

Distinct polarograms are obtained for gold in the following supporting electrolytes: 0.1 M solutions of the chlorides of potassium, sodium, lithium, ammonium, and in 0.1 M solutions of sodium nitrate, sodium perchlorate, hydrochloric, sulfuric, nitric, and perchloric acids. The nature of the ions tested has no effect on the reduction potential of gold.

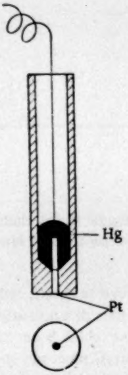

Fig. 1. Microdisc platinum electrode.

In a supporting electrolyte of 0.1 M sodium acetate, the height of the gold wave was depressed somewhat; in a supporting electrolyte of ethylamine hydrochloride the rise on the curve was steeper than in the preceding cases. A gradual drop in the wave height was observed when gold was polarographed in a supporting electrolyte of sodium tartrate. During this process, the solution acquired a violet color, presumably because of the chemical reduction of gold. A similar state of affairs was observed when Complexon III was used as a supporting electrolyte.

Changing the concentration of the supporting electrolyte from 10^{-5} to 1-2 M (as was done in the case of KCl and $NaNO_3$) while the solutions were thermostatted, has no essential effect on the wave height and on the reduction potential of gold. Some of the increase in the limiting current corresponds to the reduction of anions on the cathode [19]. In subsequent experiments the supporting electrolyte used was 0.1 and 1 M KCl.

Of particular importance in carrying out polarographic determinations with solid electrodes is the question of the repeatability of waves when successive polarograms are taken. In the case of other noble metals which we have studied [14, 18], it was shown that under certain conditions it is possible to obtain reproducible results. The definition and the reproducibility of the gold wave depends to a significant extent on the state of the surface of the microdisc electrode. The first one or two polarograms taken with a freshly prepared electrode do not appear to be sufficiently characteristic for a given gold concentration. They differ in that they have a more negative reduction potential, the shape of the wave is less distinct, and the wave height is less. The third and succeeding polarograms exhibit good reproducibility, and preserve their shape and height in the course of 15-20 polarograms.

After a large number of gold polarograms have been taken, they become somewhat distorted, probably as a result of the considerable increase in the electrode surface because of deposition of gold on it. In such cases, the electrode is treated with aqua regia or is polished with fine emery cloth. The design of the microdisc electrode permits the latter technique, which is the simplest method, to be used. Before the electrode is used it is carefully washed with distilled water, and two or three polarograms are taken which are not used for quantitative measurements. After these two or three polarograms have been taken, reproducible waves can be obtained which are suitable for analytical purposes.

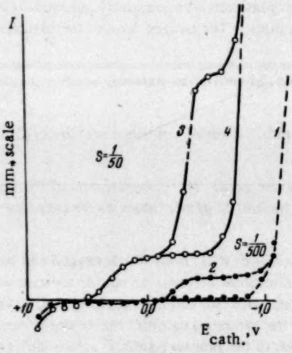

Fig. 2. Effect of oxygen on the gold wave: 1 and 2) Supporting electrolyte 0.1 M KCl before and after removal of oxygen; 3 and 4) solution containing 0.43 mg of gold in 25 ml, before and after removal of oxygen.

In order to get sharply defined polarograms for gold, and to get constant reduction potentials, it is also essential to choose conditions which will ensure that there is hardly any polarization of the platinum anode. As is evident from Fig. 4, it is only when the anode surface is large enough that its potential remains constant during the whole time that polarograms are being taken, i. e., an anode that is similar to other nonpolarizable anodes.

As shown in Fig. 5, there is a direct proportionality between the wave height of gold and the concentration of the latter in solution over a fairly wide interval of 2×10^{-4} to 3×10^{-6} M/liter.

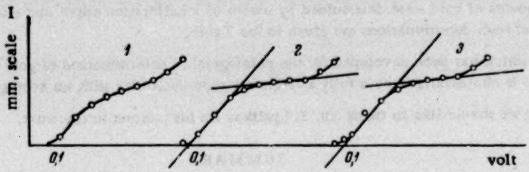

Fig. 3. Repeatability of the gold wave in successive polarograms: 1) After cleaning the microelectrode; 2) after gilding the microelectrode; 3) the tenth polarogram.

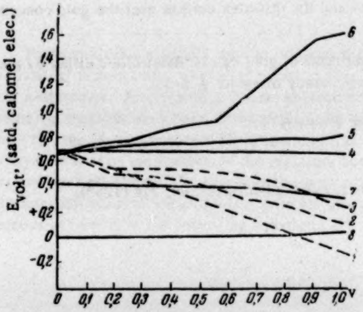

Fig. 4. Change in electrode potentials during polarographic determinations of gold: 1,2,3,) of cathode (microdisc platinum rotating electrode); 4,5,6) of anode – platinum disc with surface area of 400, 120, and 60 mm² respectively; 7 and 8) of anode – mercury, saturated calomel electrode.

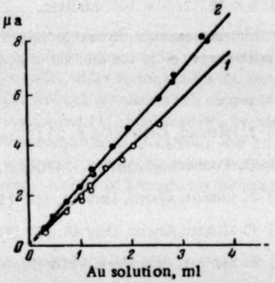

Fig. 5. Relation between the diffusion current and gold concentration when a rotating microdisc platinum cathode is used: 1) Anode – saturated calomel electrode; 2) anode – platinum disc area 400 mm². T_{Au} = 0.00043 g/ml.

Determination of Gold

Au taken, g·10^{-6}/ml	Wave ht. mm of scale**	Au found, g·10^{-6} per ml	Error		Au taken g·10^{-6}/ml	Wave ht. mm of scale**	Au found, g·10^{-6}/ml	Error	
			abs.	rel. %				abs.	rel., %
4,3	5,2	4,04*	—0,26	—6	16,2	20,3	16,0*	—0,2	—1,2
4,3	5,5	4,2*	—0,1	—2,3	21,5	27,7	22,2	+0,7	+3,3
6,0	8,8	6,3*	+0,3	+5	21,5	27,6	21,7	+0.2	+0,9
8,6	10,6	8,43	—0,17	—2	22,4	28	22,4	0,0	0,0
10,3	13	10,3	0,0	0,0	22,4	27,9	22,3*	—0,1	—0,4
12,0	14,8	11,87	—0,13	—1,1	25,8	32,5	25,8	0,0	0,0
14,6	18	14,7*	+0,1	+0,7	26,7	33,8	27,26*	+0,56	+2,1
16,2	20,5	16,2	0,0	0,0					

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* Determined by the method of additions.

** Mean of three determinations.

Unknown amounts of gold were determined by means of a calibration curve and also by the method of additions. Results of such determinations are given in the Table.

The method which has been developed for the polarographic determination of gold by means of a rotating microdisc electrode is characterized by a fully satisfactory reproducibility with an average accuracy of ± 2%.

In conclusion we should like to thank Yu. S. Lyalikov for his interest in the work.

SUMMARY

Conditions for the polarographic determination of gold solutions by means of a solid platinum microdisc rotating electrode have been studied.

It has been established that gold from chloroauric acid gives a clearly defined polarogram in various supporting electrolytes; the wave is a result of the reduction of Au^{III} to Au^0; polarographic determinations can be carried out without resorting to preliminary removal of dissolved oxygen.

There is a linear relation between gold concentration and the diffusion current over the gold concentration range of 2×10^{-4} to 3×10^{-6} M/liter.

Within the concentration range indicated, unknown amounts of gold can be determined either by means of a calibration curve, or by the method of additions, with an accuracy of about ± 2-3%.

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AMPEROMETRIC TITRATION OF MAGNESIUM WITH AMMONIUM FERROCYANIDE

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Ferrocyanides are widely used as reagents for the quantitative determination of many metals. For example, the classical ferrocyanide method of titrating zinc by means of an external indicator [1], or potentiometrically [2] is well known. Ferricyanides can be reduced on a platinum electrode, while ferrocyanides are oxidized. Amperometric methods have been developed for the determination of nickel [3], potassium [4], copper [5, 6], calcium [7], zinc [8-14], thallium [15], cadmium [8], fluorine [16], manganese [17], and lead [8], by means of ferrocyanides. The mechanism of the reactions between potassium ferrocyanide with calcium and magnesium salts has been clarified [25]. However, far from all the reactions with ferrocyanides have been studied, particularly from the point of view of using them for amperometric titration. Worthy of attention is the reaction which proceeds according to the following equation [18]:

$$Mg^{2+} + (NH_4)_4[Fe(CN)_6] = \underset{\downarrow}{\underline{Mg(NH_4)_2[Fe(CN)_6]}} + 2NH_4^+.$$

white crystalline precipitate

The necessity of studying this reaction arose, in particular, from the fact that at present there are only two known methods for the amperometric determination of magnesium; by means of 8-hydroxyquinoline [19,20], and by means of the dye pontachrome violet SW [21]. The indicator electrode used in these methods is the dropping mercury electrode, and this electrode, as is well known, is not as convenient as a platinum electrode.

TABLE 1

pH Limits for the Titration of Magnesium with Ammonium Ferrocyanide

pH	Equivalence point in terms of ml of ammonium ferrocyanide solution
2	No reaction
3	No reaction
4	No reaction
5	No reaction or proceeds very slowly
6	3.42
7	3.44
8	3.43
9	3.43

Accordingly, one of our problems was to establish the possibility of carrying out an amperometric determination of magnesium on a setup containing a rotating platinum microelectrode, ammonium ferrocyanide being used as the reagent. The diffusion current arising from the anodic oxidation of ferrocyanide is particularly convenient for amperometric titration. The normal potential of the system ferro-ferricyanide equals + 0.36 v. Other authors give different values; e. g., Latimer [22] gives a value of +0.48 v. The titration potential should be chosen with respect to the medium in which the titration is to be carried out. The reaction which we have chosen for study proceeds in an ammoniacal medium.

From published results [23], it is known that in a supporting electrolyte of ammonium chloride, the diffusion current for potassium ferrocyanide starts at 0.8 v relative to a mercury-iodide reference electrode. This potential corresponds to +0.54 v relative to the saturated calomel electrode. In our case the potential was + 0.3–0.4 v. Application of an external emf of 0.7 v ensured a diffusion current for the oxidation of ferrocyanide.

TABLE 2

Determination of Magnesium

Mg taken, mg	Mg found, mg	Absolute error, mg	Relative error, %	Mg taken, mg	Mg found, mg	Absolute error, mg	Relative error, %
5,92	5,87	—0,05	0,84	3,57	3,5	—0,07	1,96
	5,84	—0,08	1,35		3,5	—0,07	1,96
	5,84	—0,08	1,35	2,38	2,38	±0	0,0
4,76	4,69	—0,07	1,47		2,33	—0,05	2,5
	4,68	—0,08	1,68				

EXPERIMENTAL

Amperometric titration was carried out on the usual setup using a rotating platinum electrode 8 mm long and 0.5 mm in diameter fused into a glass tube with a bent tip. The latter ensured that the solution was well stirred. The electrode was rotated at a rate of 700 rpm by means of a motor. The cathode was a saturated calomel electrode connected to the titration cell via an agar-agar bridge. A galvanometer with a sensitivity of 2.6 × $\times 10^{-6}$ amp/scale division was used for measuring the current. A voltage of 0.7 v was applied to the electrodes from a storage battery. It was regulated by means of a plug rheostat and controlled by means of a voltmeter.

Ammonium ferrocyanide was prepared from pure potassium ferrocyanide. By the action of concentrated hydrochloric acid on the potassium salt, ferrocyanic acid was precipitated. On passing dry ammonia through an alcoholic solution of this acid, white crystals of ammonium ferrocyanide were deposited. The concentration of the ferrocyanide was established by titration [24].

The $MgCl_2$ titrated was 0.01 M. The concentration of the magnesium chloride solution was established gravimetrically, and also by titration with Complexon III in the presence of eriochrome black ET-00.

Preliminary experiments on the titration of magnesium chloride with ammonium ferrocyanide showed that in aqueous solution a precipitate of the ferrocyanide of magnesium and ammonium is not obtained. Accordingly, it was found necessary to resort to aqueous-alcoholic solutions, and to carry out a number of experiments in order to establish the optimum alcohol content of the solution. It was found that for an alcohol content less than 50% by volume, the precipitate formed very slowly. On increasing the alcohol content to 75%, a sharp drop in the diffusion current of the ferrocyanide is observed. Taking all these factors into account, all subsequent titrations were carried out at an alcohol content of 50% by volume of the solution.

Titration Procedure. To a measured volume of $MgCl_2$ solution contained in a 100 ml beaker was added 25 ml of 96% ethanol, and the volume adjusted to 50 ml. The magnesium was titrated with a solution of ammonium ferrocyanide measured out from a 5 ml microburet. Titration of 0.01 M magnesium chloride with 0.1M ammonium ferrocyanide showed that it is possible to determine magnesium quantitatively by this method.

During titration it was observed that there is a satisfactory linear relation between the volumes of magnesium chloride taken for titration and the amounts of ammonium ferrocyanide used in the titration; the reproducibility of the experimental results was also good.

The titration curve had the shape of two lines meeting at an obtuse angle.

Effect of pH of the Solution on the Titration Results. The potential of the ferri-ferrocyanide electrode depends on hydrogen ion concentration [2]. The oxidizing capacity increases with increasing acidity of the solution.

In order to establish the pH range within which the reaction of the formation of the ferrocyanide of magnesium and ammonium can be used for quantitative amperometric determination of magnesium, equal amounts of magnesium chloride solution were titrated at various pH values (Table 1). Theoretically, 3.48 ml of 0.1 M ferrocyanide is required to titrate the amount of magnesium (6.8 mg) taken.

The results obtained showed that amperometric titration of magnesium with ammonium ferrocyanide can be carried out at a pH of 6-9.

TABLE 3

Determination of Magnesium in the Presence of Impurities (5.8 mg Mg taken)

Taken		Ratio metal: Mg (by wt.)	Mg found, mg	Absolute error, mg	Relative error, mg
metal	mg				
Sodium	86,25	14,8	4,68	−1,12	19,13
"	57,5	9,91	5,5	−0,3	15,17
"	28,75	4,95	5,7	−0,1	1,72
"	17,25	2,97	5,73	−0,07	1,2
"	11,5	1,98	5,75	−0,05	0,86
Potassium	585	100,8	6,3	+0,5	8,62
"	390	67,24	6,2	+0,4	6,9
"	195	33,62	6,2	+0,4	6,9
Aluminum	7,5	1,29	5,74	−0,06	1,03
"	0,75	0,13	5,77	−0,03	1,51
Manganese	0,3	0,05	6,0	+0,2	3,44
"	0,1	0,017	5,8	±0	0,0
"	0,03	0,005	5,79	−0,01	0,17
Zinc	0,18	0,03	5,8	+0	0,0
"	0,018	0,003	5,76	−0,04	0,69
Copper	0,03	0,005	5,75	−0,05	0,86
Iron	0,05	0,008	5,75	−0,05	0,86
Beryllium	0,14	0,025	5,73	−0,07	1,2
"	0,014	0,0025	5,74	−0,06	1,03
"	0,0014	0,00025	5,73	−0,07	1,2

It is clear from Table 2 that with decreasing magnesium concentration the accuracy of its determination also decreases, but does not exceed 2%. In all cases the error is on the negative side. This can be explained by the fact that at the end the precipitation of magnesium proceeds very slowly. Accordingly, the reagent added at the titration endpoint remains for a long time in excess and changes the electrode potential before the equivalence point is reached.

Determination of Magnesium in the Presence of Other Elements. Next, experiments were carried out on the determination of the same amount of magnesium in solutions containing sodium, potassium, barium, aluminum, manganese, zinc, copper, iron, and beryllium salts (Table 3).

Excess of the alkali metals leads to large errors. Aluminum, even in large amounts, does not interfere with magnesium determination. Beryllium does not interfere either. The presence of ions which are precipitated by ferrocyanide – Fe^{3+}, Cu^{2+}, Mn^{2+}, Zn^{2+} – interferes with magnesium determination. However, in the presence of small amounts of these ions the error does not increase; it even decreases to some extent. This latter fact can be explained by the fact that part of the ferrocyanide is used up for precipitation, and accordingly the negative error decreases as compared with that observed in the experimental results for the determination of magnesium in pure solutions.

Thus, in the presence of aluminum, manganese, zinc, copper, iron, and beryllium, even in amounts which are greater than those that are usual for magnesium alloys, magnesium can be titrated with a sufficient degree of accuracy.

For determination of magnesium in alloys, 0.15-0.17 g of the latter is dissolved in 5 ml of HCl (1 : 1) in a 50 ml beaker. The solution is transferred to 250-ml standard flask and its volume made up to the mark with distilled water. An amount of 10 ml of the solution obtained is transferred to a 100-ml beaker and 25 ml of 96% ethanol added. The volume is made up to 50 ml and the solution titrated at a pH of 7-8 with ammonium ferrocyanide.

TABLE 4

Determination of Magnesium in Alloys

Mg found, %		Absolute deviation, %	Relative deviation, %
amperometric	complexonometric		
96,7; 96.3	97,4	−0,7: −1,1	−0,71; −1,12
89,83; 89.54	90,6	−0,77; −1,06	−0,85; −1,17
97,0; 97,0	97,4	−0,4; −0,4	−0,41; −0,41

Results for the determination of magnesium in a few samples of magnesium alloys when carried out by the suggested method and by a complexonometric method are given in Table 4.

SUMMARY

Conditions have been established for the amperometric titration of magnesium in solutions of its pure salts, and in the presence of other elements, in which a rotating platinum electrode is used and the titrant is ammonium ferrocyanide.

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A RAPID PHOTOMETRIC METHOD FOR THE DETERMINATION OF TOTAL RARE EARTHS

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Until recently the main methods for determination of the total rare earths in ores have been gravimetric ones [1, 2]. There are no satisfactory photometric methods for the determination of small amounts of these elements. The color reactions of the rare earths with aluminum [3], murexide [4], pyrogallol [5], etc., are only used for detection of these elements. Our attention was drawn to the reagent arsenazo [6] suggested by V. I. Kuznetsov for detection of the rare earths. This reagent has been used for the quantitative determination of total rare earths.

Arsenazo gives a color reaction with many metals [6, 7]. The rare earths, scandium, and yttrium, in a neutral medium give violet-colored solutions with arsenazo. Under these conditions color reactions are also given by uranium (VI), copper (II), aluminum, thorium, vanadium (IV), zirconium, gallium, indium, palladium (II) and iron (III). Solutions of the reagent itself in acid and neutral media have an orange color (λ_{max} 500 mμ), while in alkali media the color is violet (λ_{max} 530 mμ).

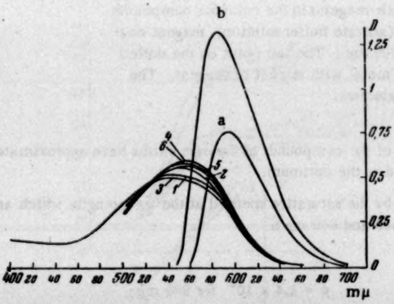

Fig. 1. Absorption curves for mixtures of 2×10^{-5} M arsenazo solution with 1×10^{-4} M solutions of the nitrates of the rare earths at a pH of 6.5: Cuvette length 10.0 mm; blank solution – distilled water: 1) Solution of arsenazo with yttrium; 2) with lanthanum; 3) with neodymium, 4) with praseodymium; 5) with a mixture of the nitrates of lanthanum, samarium, neodymium, praseodymium, gadolinium, and dysprosium; 6) with cerium; curves a and b) transmission curves for the liquid filters made from a mixture of potassium dichromate and copper sulfate solutions.

We have made a study of the properties of the reagent arsenazo and its compound with certain elements which occur in mineral raw material [7].

The reagent arsenazo behaves in solution as a sexibasic acid H_6P, two hydrogens of which dissociate from the molecule in acid solutions (K_1 is approximately 1, $K_2 = 5 \times 10^{-2}$ – this refers to the dissociation of hydrogen ions from the sulfo group); the next two hydrogen ions dissociate from the arsono group ($K_3 = 3.2 \times 10^{-4}$ and $K_4 = 3 \times 10^{-8}$), and the last two hydrogen ions dissociate in the alkaline region from the hydroxy group ($K_5 = 4.9 \times 10^{-10}$ and $K_6 = 2.9 \times 10^{-13}$). The dissociation is connected with the color change in solution.

The reactions of the rare earths were studied spectrophotometrically using SF-4 and SF-2M spectrophotometers. The pH was controlled with a pH meter using a glass electrode.

The similarity of the chemical properties of the rare earths allows one to assume that the properties of their compounds with arsenazo will coincide to a considerable extent. Solutions of the nitrates of trivalent cerium, lanthanum, praseodymium, neodymium, and yttrium were prepared for these studies, and absorption curves of the solutions of these ions with arsenazo were taken at various pH values, and for various ratios of the reacting ions.

As is evident from Fig. 1, the absorption curves of the compounds formed between these ions and arsenazo are very similar to each other; the maximum varies within the limits 540-560 mμ.

A study of the relation of the optical densities of the solutions of the complexes to the pH showed that they start to form at pH 2.5-3.0. The optical density of the solutions then increases up to a pH of 5.5-6.5, after which it remains constant in the pH range 7.0-9.0. Further increases in the pH lead to the formation of the alkali form of arsenazo which has a violet color in solution; solutions of the compounds of the rare earths have approximately the same color. The pH range 6.0-7.5 may be regarded as the optimum.

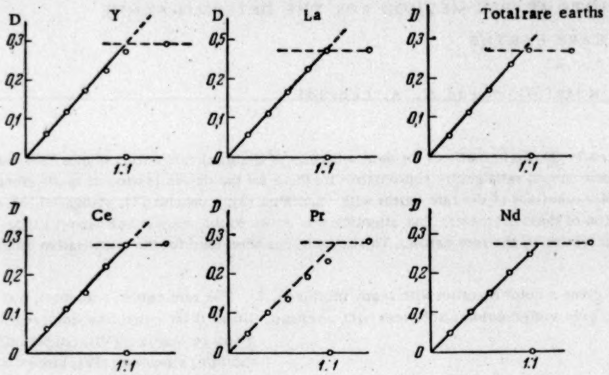

Fig. 2. Determination of the ratio of metal: reagents in the complex compounds of arsenazo with the rare earths at pH 7.0 (acetate buffer solution), reagent concentration of 2×10^{-5} mole; wavelength 600 mμ. The last point on the dotted line corresponds to a tenfold excess of the metal with respect to reagent. The metal: reagent ratio is plotted along the abscissa.

The molar extinction coefficients were determined by the saturation method at the wavelengths which are most convenient for the practical use of these reactions (580 and 600 mμ):

For the compound of cerium with arsenazo
$\epsilon = 2.4 \times 10^4$ for 580, $\epsilon = 1.4 \times 10^4$ for 600 mμ;

for the compound of lanthanum
$\epsilon = 2.35 \times 10^4$ for 580, $\epsilon = 1.35 \times 10^4$ for 600 mμ;

for the compound of neodymium
$\epsilon = 2.5 \times 10^4$ for 580, $\epsilon = 1.5 \times 10^4$ for 600 mμ;

for the compound of praseodymium
$\epsilon = 2.45 \times 10^4$ for 580 $\epsilon = 1.45 \times 10^4$ for 600 mμ;

for the compound of yttrium
$\epsilon = 2.25 \times 10^4$ for 580, $\epsilon = 1.35 \times 10^4$ for 600 mμ.

Experiments in which the concentration of one ion was varied while the concentration of the other was kept constant [8] showed that reagent ions and element ions form a compound in which they are in the molar ratio of 1 : 1 (Fig. 2). An analysis of the curves expressing the relation between formation of the colored compound and pH by calculating the bilogarithmic relation between the logarithm $\frac{[Me]_{complex}}{[Me]_{free}}$ and pH, where [Me] is the concentration of the ions of one of the elements in the complex compound and in the free state [8], showed that all the reactions are of the same type, i. e., one hydrogen atom is split off for one complex ion of the colored compound (Fig. 3). The equilibrium was studied at a pH of 3.0-6.0, i.e., under conditions which ensure only insignificant hydrolysis of the ions of the rare earths ($pK_{hydrolysis}$ has a value of 8.5-10 for the rare earths). Accordingly, the reaction indicated can be explained by substitution of one hydrogen ion by a metal ion in the reagent molecule. In this case the equation of the reaction of an ion of a rare earth element with a reagent ion will have the following general form:

$$\underset{C_1-C}{Me^{3+}} + \underset{C_2-C}{HxP^{-(1-x)}} \rightleftarrows [Me\,(\underset{C}{H}\,x-1P)^{-(6-x-1)}\,] + H^{+}, \qquad K_{eq} = \frac{C\cdot[H^{+}]}{(C_1-C)\,(C_2-C)},$$

where C is the concentration of the colored complex.

The values of the equilibrium constant for the reactions which proceed according to this equation are approximately equal to each other for all the rare earths. Thus, the calculated equilibrium constants for the formation of the complex compounds of a series of elements with arsenazo proved to be the same; for lanthanum 1.2; for cerium 1.6; for praseodymium 1.6; for neodymium 1.5; and foryttrium 1.8.

From the expression for the equilibrium constant of the general equation of the reaction one can see that $K_{equilibrium} = \frac{K_{dissoc}}{K_{instab}}$ where K_{instab} is the instability constant of the complex, while K_{dissoc} is the dissociation constant of the reagent, as a result of which the hydrogen ion which is replaced by a metal ion splits off. The ions of the rare earths replace the hydrogen in the arsenazo, and the hydrogen splits off in an alkaline medium (the dissociation equation is characterized by the constant 4.9×10^{-10}). This is substantiated by the fact that the breakdown of the colored complexes occurs in a fairly alkaline medium (pH > 9.0). The questions of the equilibrium and stability of arsenazo complexes have been studied in more detail earlier [9]. From this it is easy to calculate the values of the instability constants of the colored complexes $K_{instab} = \frac{4.9 \times 10^{-10}}{K_{equilibrium}}$. with arsenazo, the instability constant has a value of 4.1×10^{-10}; while for the cerium compound it is 3.1×10^{-13}, for neodymium 3.3×10^{-10}, for praseodymium 3.1×10^{-10}, and for the yttrium compound 2.7×10^{-10}.

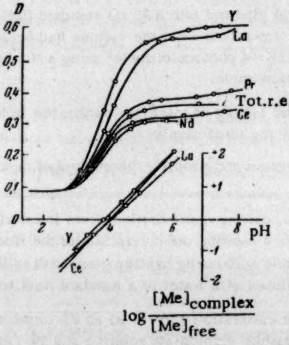

Fig. 3. Relation between the optical density of mixtures of solutions of arsenazo with the rare earths and the pH at 580 mμ, cuvette length 10.0 mm; blank solution-distilled water. Arsenazo concentration is 3.2×10^{-5} M; lanthanum and yttrium concentration 3×10^{-5} M; cerium, neodymium, praseodymium, and total rare earths concentration 1.5×10^{-5} M; determination of the order of the relation between $\log\frac{[Me]_{complex}}{[Me]_{free}}$ and pH.

Construction of a calibration curve for determining the sum of the elements of the cerium group can be carried out either on the basis of mixtures of the salts of these elements or on the basis of any one individual salt. It is most convenient for this purpose to use the nitrate of trivalent cerium, in view of its availability and in view of the possibility of checking the cerium concentration oxidimetrically or photometrically (peroxide method).

Described below is a technique for the colorimetric determination of the total rare earths of the cerium group on the basis of a calibration curve constructed with the aid of the nitrate of trivalent cerium.

The curve was constructed as follows: An amount ranging from 0.010 to 0.250 mg of cerium, in the form of a neutral standard solution, at intervals of 0.02 mg, was introduced into 25 ml standard flasks; 5-10 drops of 20% urotropine was added to each flask, followed by 2 ml of 0.1% arsenzao solution. The volume was made up to the mark with water and the solutions thoroughly mixed; the optical density was then measured on a photocolorimeter using liquid light-filters,* water being used as the reference (blank) solution. Altering the order in which the reagents are added has no effect on the path followed by the calibration curve.

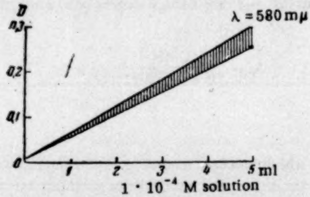

Fig. 4. The nature of the scatter in the calibration curves for various rare earths, constructed on a SF-4 spectrophotometer at a wavelength of 580 mμ and using a 10 mm cuvette.

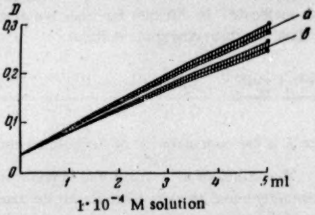

Fig. 5. Calibration curves constructed with a FÉK-M photocolorimeter using a 10 mm cuvette and liquid filters a and b; middle lines-curves for determining total rare earths.

In order to determine total rare earths, their oxides, obtained after calcining the oxalates, or their sulfates – after evaporation of the fluorides with sulfuric acid – were dissolved in the minimum amount of hydrochloric acid (sometimes it is necessary in order to get more complete solution to add hydrogen peroxide). The solution was made up to the mark in a standard flask. An aliquot was pipetted into a 25 ml standard flask; it was neutralized with urotropine, and 2 ml of 0.1% arsenazo solution was added; after the volume had been made up to the mark with water, the optical density was measured on a FÉK-M photocolorimeter using a liquid filter. The content of the rare earths was then determined from the calibration curve.

During the determination of 0.015, 0.046, 0.078, 0.155, and 1.0 mg of total rare earths, the following amounts were actually found: 0.014, 0.048, 0.075, 0.160, and 1.0 mg respectively.

The method developed makes it possible to appreciably shorten and simplify the method of determining the rare earths.

Decomposition of samples and separation of the rare earths, calcium, and thorium from interfering elements were carried out by fusion with potassium bifluoride and then washing the precipitate of the fluorides with dilute hydrofluoric acid. After converting the fluorides into soluble sulfates by heating them with sulfuric acid to dryness, and then dissolving the sulfates, the test solution is diluted with water in a standard flask to the mark.

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* The following liquid light-filters were used for constructing the calibration curves: a) an 8% solution of potassium dichromate and a 2% solution of cupric sulfate; b) 10% potassium dichromate solution and 1% cupric sulfate solution. A mixture of the solutions to be used for making the light filters was poured into a 2 cm cuvette (for light filter a) and into a 5 cm cuvette (for light filter b). The cuvettes were set up between the light source and the neutral filters of the FÉK-M photocolorimeter. The transmission curves of the light-filters are shown in Fig. 1. In Fig. 5 are shown the calibration curves for solutions of the rare earths with arsenazo for the two light-filters whose composition has been described above. The calibration curves indicate a linear relation between the optical density of the solution and the concentration of the test element, and have almost identical slopes for all the rare earths; this confirms the possibility of a quantitative determination of total rare earths.

The rare earths were determined by measuring the optical density of an aliquot of the test solution with arsenazo at a pH of 6.0-7.0.

When the test solution contains thorium, the latter can be determined at a pH of 1.6-1.8 at which the rare earths do not give colors; the amount of the latter (at pH 6.0-7.0) are determined b difference. In this way it is possible to determine the rare earths in the presence of 20-30 times their amount of thorium. The effect of aluminum and iron (III), part of which are precipitated with the fluorides, can be eliminated by addition of sodium sulfosalicylate (2-3 ml of 25% solution for 25 ml test solution) and ascorbic acid (0.1-0.2 g per 100 ml of test solution).

A determination takes 8-10 hours instead of the 3-4 days necessary for the gravimetric method. Below are given results of the determination of total rare earths in ores by the gravimetric oxalate method and by the suggested method: the following values in percent were found by the gravimetric oxalate method: 2.40, 0.20, 0.36, 0.14, and 0.08 whereas the values found photocolorimetrically were respectively; 2.38, 0.20, 0.38, 0.16, and 0.09.

The results obtained show that the technique suggested is suitable for the rapid determination of total rare earths.*

It should be noted that the sensitivity of the determination of total rare earths in natural objects is limited, both in the gravimetric method, and in the suggested colorimetric method, by the appreciable solubility of the oxalates of these elements.

SUMMARY

Compounds of the rare earths and certain other elements with arsenazo have been studied. The spectral characteristics of solutions of these compounds have been studied. The spectral characteristics of solutions of these compounds have been studied, and the values of the molar extinction coefficients of the complexes and the equilibrium constants of the reactions for the formation of these complexes have been established. It has also been established that the sensitivity of the reaction of the rare earths with arsenazo, the stability of the compounds formed, and their absorption curves are similar to each other.

A technique is suggested for constructing calibration curves for determination of the rare earths on a FÉK-M photocolorimeter with liquid light filters. A method has been developed for the photometric determination of total rare earths in natural objects.

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* The possibility that, in principle, arsenazo can be used for the quantitative determination of total rare earths has been confirmed by F. G. Zaikovskii, and V. S. Bashmakova [Zhur. Anal. Khim. 14, 50 (1959)].

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QUANTITATIVE DETERMINATION OF YTTERBIUM IN THE PRESENCE OF LARGE AMOUNTS OF ERBIUM BY OSCILLOGRAPHIC POLAROGRAPHY

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The method mainly used for the analysis of mixtures of the rare earths is the x-ray spectrographic method, which permits determination of up to 0.1% of a rare earth element with an error not greater than ± 15% [1]. Several papers have been devoted to the spectrophotometric determination of these elements: Vickery [2] studied the absorption spectra of Pr, Nd, Sm, Gd, Dy, Yb, and Er. In particular, a spectral method permits determination of up to 0.05% Yb in a mixture of the rare earths with an error not greater than ± 10% [3].

Recently, papers have appeared on the determination of the rare earths, and, in particular, of more than 5% ytterbium in the presence of elements of the yttrium subgroup, by a polarographic method; Laitinen and Taebel [4] have studied its reduction in 0.1 N NH_4Cl and found a halfwave potential $\varphi_{1/2} = 0.415 \pm 0.003$ v with respect to the saturated calomel element. Reduction only proceeds as far as the divalent state; a second wave caused by reduction of Yb^{2+} is not observed in this medium. Laitinen [5] has shown that ytterbium is reduced reversibly on a dropping mercury cathode. Holleck [6] has determined up to 0.1% Yb in a mixture of the rare earths. However, the sensitivity of the method is appreciably reduced when erbium and thulium are present in the mixtures.

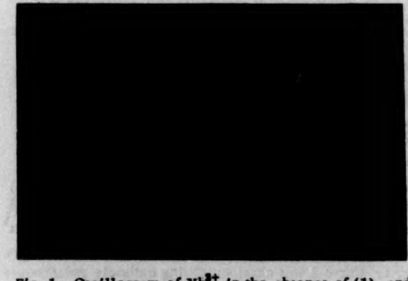

Fig. 1. Oscillogram of Yb^{3+} in the absence of (1), and in the presence of (2) large amounts of erbium; single sweep with a lag of 1.15 sec after the drop has broken off. $U_{=} = -1.00$ v, $U_{\sim} = 0.744$ v.

Barton and Kurbatov [7] have studied the relation of the diffusion current of ytterbium to the nature of the supporting electrolyte, and the relation of this current to the pH. Using ammonium chloride and lithium chloride as the supporting electrolyte, they found that the diffusion current is independent of the pH in the pH range 3.5-6.0. In 0.1 N LiCl the authors also observed a wave for the reduction of divalent ytterbium to the metal, with a halfwave potential $\varphi_{1/2}$ of 2.00-2.07 v.

In the work described here reduction of ytterbium on a dropping mercury cathode in the presence of large amounts of erbium was studied. The current was measured on an oscillographic polarograph of the GEOKhI type and on a Heyrovsky-type recording polarograph. The electrolyzer used had a volume of 3 ml. The reference electrode was a saturated calomel element. The solutions of ytterbium and erbium were prepared from the spectrographically pure oxides and from twice distilled hydrochloric acid. The supporting electrolyte – 0.1 N NH_4Cl – was prepared from the recrystallized salt. A pH of 4 was established by addition of ammonia and was controlled by means of a pH meter fitted with a glass electrode.

At concentrations greater than 25 γ/ml, ytterbium gave clearly defined waves on the Heyrovsky polarograph. However, determination of ytterbium became impossible as soon as a small amount of erbium was added to these solutions. Addition of erbium favors a sharp increase in the current at a potential close to the halfwave potential $\varphi_{1/2}$ of ytterbium. In order to overcome this difficulty we adopted oscillographic polarograph [8].

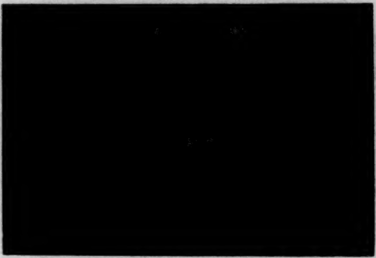

Fig. 2. Oscillogram of Yb^{3+} in the presence of large amounts of erbium in 0.1 N NH_4Cl and at a pH of 4; single sweep with a lag of 1.15 sec after the drop has broken off $U_= = -1.0$ v, $U_\sim = 0.744$ v.

Fig. 3. Oscillogram of Yb^{3+} in the presence of 1 mg Er/ml in 0.1 N NH_4Cl at pH 4; single sweep with a lag of 1.15 sec after the drop has broken off. $U_= = -1.0$ v, $U_\sim = 0.744$ v.

An oscillographic polarograph permits ready determination of the degree of reversibility of electrode processes. For this purpose use is made of the difference between the peak φ_p and halfpeak $\varphi_{p/2}$ potentials, which for reversible processes is of the form:

$$\varphi_{p/2} - \varphi_p = \frac{0.057}{n}, \tag{1a}$$

while for irreversible processes it is of the form

$$\varphi_{p/2} - \varphi_p = \frac{0.048}{n\alpha} \tag{1b}$$

Here, n is the number of electrons participating in the reaction; α is the transport coefficient. The relation (1b) is fulfilled at $\alpha < 1$. By studying the cathodic waves of Yb^{3+} it was found that its reduction to the divalent state is reversible on a dropping mercury cathode. The difference between $\varphi_{p/2}$ and φ_p was found to be 0.055 v which is close to the theoretical value. In the presence of large amounts of erbium the process becomes less reversible, as is evident from the two oscillograms of ytterbium in Fig. 1. Curve 1 was obtained during cathodic polarization and for one sweep in 0.1 N NH_4Cl, containing 25 γ Yb^{3+}/ml; the highest sweep potential exceeded the reduction potential of ytterbium and was equal to 1.744 v. The oscillogram in Fig. 2 was taken under the same conditions, but in this case the solution contained 25 mg Er/ml, i. e., in an amount 1000 times that of the ytterbium. In both cases the ytterbium waves are equally well expressed, but the slope of the wave is less, and the peak is absent on the second oscillogram.

In the oscillogram in Fig. 2, a comparison is made of the current of the supporting electrolyte 0.1 N NH_4Cl + + 25 mg Er/ml (Curve 1) and the current of the supporting electrolyte containing 25 γ ytterbium/ml (Curve 2). For average amounts of erbium, when its concentration is 10-200 times that of ytterbium, the current and the concentration of the latter are directly proportional; this follows from a comparison of the curve in Fig. 3, which corresponds to 10 γ Yb^{3+}/ml and 1 mg Er/ml, with the lower curve in Fig. 1 which was taken for the case of 25 γ Yb^{3+}/ml in the absence of erbium. Despite the presence of erbium in the first case, the ratio of the peak heights remains the same as if the erbium content in both cases were equal.

In order to compare the cathodic and anodic waves of ytterbium in 0.1 N NH_4Cl, experiments were carried out to study the effect of the rate of change of potential $\underline{v}$ on I_{max} for ytterbium. A single sweep was applied to the electrolytic cell, with a lag of 2.5 seconds after the drop had broken off. The results are shown graphically in Fig. 4. Curve 1 was obtained during cathodic polarization, while Curve 2 was obtained during anodic polarization. A comparison shows that the maximum currents coincide in both types of polarization for a rate of potential change of 1.56 v/sec. With an increasing rate of potential change the cathodic wave increases more rapidly than the anodic wave, and at a rate of 20.3 v/sec exceeds the latter by 58%. The lag of the anodic process with respect to the current is coupled with the undesirable effect of the background current on the anodic peak of ytterbium, the height of which changes strongly for an insignificant change in the erbium content of the solution. Different "current-potential" curves correspond to the same ytterbium concentration (Fig. 5). One of these curves corresponds to a content of 1.3 mg Er/ml in solution while the other corresponds to a content of 3.0 mg Er/ml. During cathodic polarization, the background has almost no effect on the ytterbium current. This means that cathodic polarization is more convenient for analytical purposes than anodic polarization. All the results given below were obtained during cathodic polarization and for one sweep. It has also been established that dissolved oxygen has no effect on the maximum current of ytterbium.

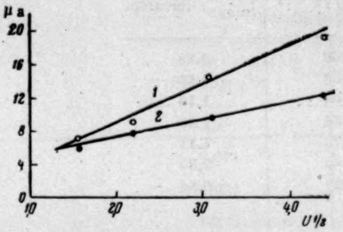

Fig. 4. Effect of the rate of potential change on I_{max} of ytterbium at 25°; 100 γ Yb^{3+}/ml in 0.1 N NH_4Cl, pH = 4. 1) Cathodic polarization at $U_{=}$ = -1.0 v and $U_{\sim}$ = 0.744 v; 2) anodic polarization at $U_{=}$ = 1.744 v and $U_{\sim}$ = = 0.744 v.

It was pointed out above that for a ratio of erbium to ytterbium concentration of the order of a few hundred, the ytterbium current is directly proportional to its concentration. Since, at higher ratios (of the order of thousands) there is deviation from linearity, it is expedient to consider both groups of ratios separately. Given in Table 1 is the relation between the maximum current of ytterbium and its concentration when the amount of erbium present is 20 to 400 times that of the ytterbium.

At ratios of Er/Yb greater than 400 and for higher lags in the impulse, the deviation from linearity becomes perceptible. They are caused by long accumulation of side reaction products near the electrode surface. Cutting down the lag eliminates this cause and enables one to reestablish proportionality. Table 2 contains results for higher ratios of Er/Yb. The lag in the impulse was small in these experiments (1.15 sec). A change in the lag, and consequently, in the surface of the drop leads to a change in current. Since the simplest method of determining ytterbium concentration in this instance is a calculation based on additions, the value of the electrode surface is not required. However, if for some other reasons it is required, a switch over from one lag to another is accompanied by a correction for the distortion of the spherical shape of the drop. For apparatus with a discrete change in the lag this distortion is the same for most solutions and can be determined once for each of its values.

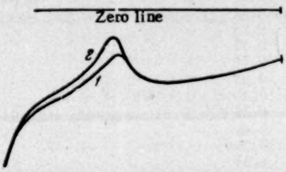

Fig. 5. Anodic curves "current-potential" for 10 γ Yb/ml in the presence of various concentrations of erbium: 1) 1.3 mg Er/ml; 2) 3.0 mg Er/ml. $U_{=}$ = = - 1.744 v and $U_{\sim}$ = 0.744 v; single sweep with a lag of 2.5 seconds after the drop has broken off.

Experimental procedure. An amount equal to 200-700 mg of Er_2O_3 containing ytterbium as an impurity is dissolved in 5 ml of concentrated hydrochloric acid. The solution is evaporated on a sand bath almost to dryness; the residue is dissolved in distilled water and the solution transferred into a 10-20 ml standard flask. By adding a few drops of concentrated ammonia and a solution of ammonium chloride, the concentration of the latter is established at 0.1 N, while the pH is 4.

TABLE 1

The Reaction between the Value of I_{max} for Yb^{3+} and the Concentration of the Latter in 0.1 N NH_4Cl, at a pH of 4 in the Presence of Erbium (single sweep; v = 4.8 v/sec; lag after drop has broken off 5.15 sec)

Yb concentration, γ/ml	Er concentration, mg/ml	Er/Yb	I_{max}, microamp.
2.5	1.0	400	0.28
5.0	1.0	200	0.60
10.0	1.0	100	1.16
10.0	1.2	120	1.20
10.0	2.7	270	1.17
25.0	1.0	40	2.80
50.0	1.0	20	5.54

TABLE 2

The Relation between the Value of I_{max} for Yb^{3+} and the Concentration of the Latter in 0.1 N NH_4Cl, at a pH of 4 in the Presence of Erbium (lag after a drop has broken off 0.15 seconds)

Yb concentration λ ml	Er concentration, mg/ml	Er/Yb	Polarization rate, sec	I_{max}, microamp
10	5,0	500	2,45	0,26
10	5,0	500	4,80	0,37
			9,50	0,57
			20,30	0,65
10	10,0	1000	2,45	0,26
			4,80	0,36
			9,50	0,59
10	15,0	1500	2,45	0,26
			4,80	0,35
			9,50	0,57
			20,30	0,71
10	25,0	2500	2,45	0,25
			4,80	0,35
			9,50	0,54
20	15,0	750	2,45	0,49
			4,80	0,75
			9,50	1,06
			20,30	1,46
20	25,0	1250	2,45	0,48
			4,80	0,72
			9,50	0,98
			20,30	1,40
30	25,0	833	2,45	0,81
			4,80	1,09
			9,50	1,65

An amount equal to 1 ml of this test solution is introduced into the electrolyzer, a constant voltage (-1.0 v) is applied to the cell together with a single sweep with a known amplitude (about 0.8 v), the time lag being about 1 second. The oscillograms of the supporting electrolyte, the test solution, and the solution to which additions have been made are taken from the screen onto tracing cloth, after which, using a published method [9], the currents are determined, and the ytterbium concentration calculated.

Our interest is the determination of less than 0.1% Yb in erbium samples, for which the accuracy of the x-ray spectrographic method drops sharply, and amounts to 50%; results of both methods are compared in Table 3.

TABLE 3

Polarographic and X-Ray Spectrographic Analysis of Erbium Samples

Ytterbium found, %		Deviation, %
by oscillographic polarography	by x-ray spectrography	
0.25	0.23	+ 8.7
0.095	0.15	−36.7
0.020	Not detected	−
Not detected	" "	−

The results given in Table 3 show that during determination of traces of ytterbium in erbium, the sensitivity of oscillographic polarography is almost one order higher than that of the x-ray spectrographic method, although the experimental error does not exceed 11%. For Yb contents greater than 0.1% good agreement is observed between the results of both methods.

Oscillographic polarography is also suitable for the determination of ytterbium in samples containing a large amount of yttrium earths.

SUMMARY

Determination of ytterbium is not possible in the presence of erbium when an ordinary polarograph is used. A method has been developed for the quantitative determination of Yb^{3+} in erbium samples by means of oscillographic polarography. When traces of ytterbium are determined the sensitivity of the method is almost an order higher than the sensitivity of x-ray spectrographic analysis; the accuracy of the determination is 11%. At a concentration of Yb^{3+} higher than 0.1% the results obtained by both methods are in good agreement.

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THE PHOTOMETRIC DETERMINATION OF TIN

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Quercetin, hematoxylin, and stilbazo can be used for the photometric determination of microamounts of tin [1]. Hematoxylin has been used as a reagent for the determination of tin by Tartakovskii, Charlot, Teicher, and Gordon [2, 3, 4]. Determination of tin with hematoxylin is possible in an acid medium [2]. The sensitivity of the method amounts to 500-700 μg in 50 ml of solution. Solutions of the complex compound of tin with hematoxylin do not conform to the Lambert-Beer law [4]. Photometric determination of tin with quercetin is carried out in a solution with an acidity of 0.2 N [5]. The composition of the compound of tin with quercetin corresponds to the ratio Sn : quercetin = 3 : 2 [5]. Recently a paper has been published on the photometric determination of tin in steel and in iron metal [6] at a pH of 3.0-3.3 by means of quinalizarin. The Lambert-Beer law is obeyed. Tin is removed from iron by coprecipitation with manganese dioxide. The precipitate of MnO_2 is dissolved in a mixture of hydrochloric acid and H_2O_2.

In the present article some examples are given of the photometric determination of tin by means of quercetin, hematoxylin, and stilbazo. Detailed spectral characteristics of the complex compounds of tin with the reagents indicated have been published previously [1].

Determination of Tin in Nickel Metal by Means of Quercetin. The permissible tin content of nickel Marks N-O and N-1 is 0.0003-0.001%. According to GOST-634-56, the tin content of samples of nickel of these marks should be determined by iodometric titration using a sample of 25 g. When the tin content is 10^{-3}-10^{-4}%, such determination exhibits poor reproducibility. Moreover, the determination must be carried out on large aliquots which is not always convenient and possible. For the quantitative determination of tin in nickel Marks N-O and N-1, we have used a colorimetric method based on formation of the lemon-yellow colored compound of tin with quercetin.

The compound of tetravalent tin with quercetin is extracted from the aqueous phase with a 1 : 1 mixture of isoamyl alcohol and ether. Free quercetin is also extracted by this solvent, but the color of its extracts is considerably weaker than the color of the extracts of the quercetin-tin complex.

When the quercetin concentration of the aqueous phase is 5×10^{-4} mole, the organic solvent layer is colorless. The sensitivity of the reaction of quadrivalent tin with quercetin is 1 γ of tin in 25 ml of the aqueous phase when extraction is used. Extraction of the complex compound of tin with quercetin is particularly effective when it is used for determination of tin in metals whose salts form intensely colored solutions (nickel and chromium).

During these determinations of tin, the elements which interfere most are antimony and iron. Many other elements such as Hg, Ag, As, Al, and Bi do not interfere with the determination of tin by means of quercetin. Interference from iron can be avoided by reducing the iron with thiourea; antimony does not interfere with tin determination if the antimony content does not exceed 20 γ in the sample.

The nickel we used for our tests was nickel which had been purified for special purposes.

Tin was determined in nickel metal as follows. An amount equaling 1 g of nickel was dissolved in hydrochloric acid. A proportion of 1 : 1 nitric acid was added dropwise to accelerate the dissolution. After the sample had dissolved, the solution was evaporated to a volume of 5-10 ml; 5-6 ml of a saturated solution of thiourea was added, and the solution was neutralized with 4% sodium hydroxide until a permanent turbidity was obtained. To the solution was added a drop of 1 N hydrochloric acid, 1 ml of a 10^{-3} M alcoholic solution of quercetin, and acetate buffer solution with a pH of 4-5 until the volume reached 25 ml. The mixture was allowed to stand for 5 minutes and then was transferred to a separating funnel. Then, 5 ml of a mixture of isoamyl alcohol and ether was added to the contents of the funnel and the whole thoroughly shaken. After the two layers had separated out and the water layer had been removed, the color of the organic solvent layer was compared with that of a series of standard solutions prepared in the same way. Less than 1 γ of tin was found in 1 g of the test nickel. In order to check on the method, a series of determinations was carried out in which known amounts of tin were added to this same sample of nickel. The results obtained are given in Table 1.

TABLE 1

Weight of nickel taken, g	Tin added, γ	Tin found:		Relative error	Weight of nickel taken, g	Tin added, γ	Tin found:		Relative error
		γ	%				γ	%	
0.8	–	1	$\sim10^{-4}$		0.8	3	4.0	$5.0\cdot10^{-4}$	+ 7
0.8	–	1	$1.2\cdot10^{-4}$		0.8	6	6	$7.5\cdot10^{-4}$	-11
1.6	–	1.5	10^{-4}		0.8	2	2.5	$3.1\cdot10^{-4}$	- 9
0.8	4	4.5	$5.6\cdot10^{-4}$	-5	1.6	4	5	$3.1\cdot10^{-4}$	- 9

Sample weights of 1 g are sufficient for determination of tin in nickel when the tin content is of the order of 10^{-4}%. When the tin content is higher, the weight of sample taken can be reduced accordingly. The experimental error is fully permissible for the determination of such small amounts. The method is simple to carry out, does not require large amounts of sample, and does not take very long; a determination can be carried out in 1.5-2 hr.

Determination of Tin in WO_3 by Means of Stilbazo. Quadrivalent tin forms an orange-colored compound with stilbazo [7]. On the basis of this reaction, we have developed a photometric method for the determination of tin in tungsten-nickel, in molybdenum-nickel alloys, and in WO_3.

Stilbazo forms colored compounds with many elements including iron, aluminum, copper, etc. Removal of tin from the other components of the alloy was effected by distilling it as its bromide according to an accepted method [8].

Concentration of tin in the distillate was effected by coprecipitating tin with copper sulfide. Coprecipitation of tin with copper sulfide is used for the determination of tin in nickel-based alloys [8].

Tin was determined in WO_3 as follows. About 2.5 g of WO_3 was dissolved in 8 ml of 30% sodium hydroxide on heating. After the WO_3 had dissolved, 60 ml of 30% tartaric acid and 0.15 ml of cupric nitrate containing 100 mg of copper/ml were added to the solution. The pH of the solution obtained was adjusted to 2 using indicator paper; the solution was heated almost to the boil and hydrogen sulfide passed for 20 minutes through the hot solution. The precipitated sulfides were filtered off, and washed with hydrogen sulfide water; cupric nitrate solution was added to the filtrate and the precipitation repeated.

Experiments showed that if the sulfides are not precipitated the second time, the loss of tin amounts to approximately 30% of the total tin.

The sulfide precipitate on the filter was treated with 5-6 ml of hot 1 M sodium hydroxide. The same portion of solution was passed through the precipitate of the sulfides 7-10 times. During this process some of the copper dissolves but the extraction of tin from the precipitate is complete. A saturated solution of thiourea was used for complexing the copper as a colorless complex. A quantity equaling 0.5 ml of a 0.05% aqueous solution of stilbazo was added to the final solution; excess alkali was neutralized with dilute hydrochloric acid until the color of the solution changed from red to orange; buffer solution with pH 5 was then added to bring the volume up to the requisite value.

TABLE 2

Sample No.	Tin added, γ	Total tin found, γ	Relative error, %
1	–	12	–
1	5	16	− 6
1	8	18	−10
2	–	11	–
2	15	24	− 7

The color of the solutions obtained was compared with that of standard solutions containing 5-20 γ of tin in a 25-ml solution.

Determination of tin in various samples of WO_3 was checked by the suggested method. The accuracy of the method was checked by the method of additions. The results obtained are given in Table 2.

Tin was also determined in three samples of WO_3 by this method; the tin being also determined spectrographically as a control. The results of these determinations are given in Table 3.

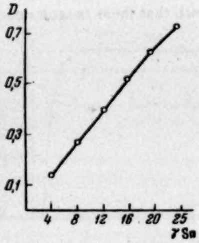
The experimental error for the determination of tin by means of stilbazo does not exceed the error normally permissible in colorimetric determinations.

Determinations of tin in W-Ni alloys by means of stilbazo is possible for tin contents of the order of 10^{-4}% using sample aliquots of about 2 g.

Determination of Tin in Bronze by Means of Hematoxylin. For determination of tin in bronze we used a method based on formation of a violet-colored compound between quadrivalent tin and hematoxylin.

Determination of tin in a standard sample of bronze 68-a was carried out by the following technique.

A quantity equaling 2 g of bronze was dissolved in nitric acid containing a small amount of hydrochloric acid. After the aliquot had dissolved completely, and the nitrogen oxides had been removed by boiling, the volume of the solution was made up to 100 ml; this solution was neutralized with sodium hydroxide solution until a turbidity was obtained which dissolved on addition of a few drops of acid; tin was then precipitated with manganese dioxide. Coprecipitation of tin with manganese dioxide was carried out twice. The manganese dioxide was dissolved in the minimum possible amount of hot 1 : 2 hydrochloric acid. An aliquot of this solution, containing about 10 γ of tin, was transferred to a colorimeter tube; formalin was added to reduce elemental chlorine, and the solution was neutralized with sodium hydroxide solution until a turbidity was obtained which was dissolved on dropwise addition of 1 N hydrochloric acid. To the solution obtained wad added 2 ml of a saturated solution of thiourea, and 0.5 ml of 10^{-3} M hematoxylin solution, and a buffer solution with a pH of 4 or 3 added to bring the volume up to a definite value (15-20 ml). After 10 minutes the light absorption of the solution was measured on a FM-1 photometer using a No. 4 light-filter.



Calibration curve for determination of tin by means of hematoxylin.

The calibration curve for determination of tin by means of hematoxylin is shown in the diagram.

This technique can be recommended for the determination of tin at levels of 10^{-5}-10^{-4} %.

TABLE 3

Sample No.	Tin found, %	
	photometrically	spectrographically
1	$3 \cdot 10^{-4}$	$3 \cdot 10^{-4}$
2	$5 \cdot 10^{-4}$	$5 \cdot 10^{-4}$
3	$4 \cdot 10^{-4}$	$4 \cdot 10^{-4}$

For determination of tin of the order of 10^{-2}% in bronze, the technique for determining tin can be simplified considerably. An amount of 0.05-0.1 g of bronze is dissolved in the minimum amount of nitric acid (1 : 1) containing HCl, and the solution evaporated to a small volume. The solution obtained is transferred to a colorimeter tube in which it is neutralized with alkali until the color of the solution changes from bright-blue to a greenish-blue; 2 ml of a saturated solution of thiourea is then added to complex the copper; this is followed by 0.5 ml of hematoxylin solution, and buffer solution is finally added to bring the volume up to 15 ml. For bronze mark AMZh, a buffer solution with a pH of 3 should be used. After standing for 10 minutes, the optical density is measured on a FM-1 photometer using a No. 4 light-filter.

TABLE 4

Specified tin content	Tin found in 2 g samples by precipitation with MnO_2, %	Tin found on 0.05 g samples without preliminary separation, %
0.03%	0.029; 0.031; 0.029	0.032; 0.032; 0.031

Determination of tin in bronze 68- a was carried out by the two variants of the technique suggested. The results obtained are given in Table 4.

SUMMARY

Methods have been developed for the photometric determination of tin in nickel metal marks N-0 and N-1, in WO_3, and in bronze, using quercetin, stilbazo, and hematoxylin. It has been shown that these reagents can be used for the determination of microamounts of tin.

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SEPARATION OF NIOBIUM AND TANTALUM BY LIQUID EXTRACTION

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The current methods for the separation of niobium and tantalum suffer serious disadvantages, the chief of which are the complexity and duration of time taken to carry out such methods. The time taken is connected with the necessity of repeated operations, as in the classical method of Marignac [1] for example. The most widely used methods are the method of fractional precipitation with tannin in an oxalate medium [2, 3], the hypophosphite [4] and iodate [5] methods, precipitation with phenylarsonic acid [6, 7], and also chromatographic separation [8-12]. Recently, the extraction method of separating these elements which is characterized by high selectivity, simplicity, and the short time required has attracted attention. A number of papers have been published on this question [13-25]. In our work we have considered the extraction of the fluoride complexes of niobium and tantalum with tributylphosphate (TBP), which permits separation of these elements at fairly low concentrations of hydrofluoric acid. The problem we tried to solve was to develop analytical and preparative methods of separating these elements using a continuous counterflow extraction column.

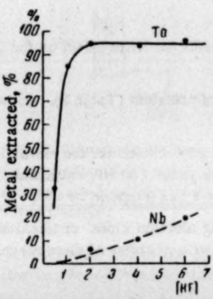

Fig. 1. Percentage extraction of niobium and tantalum from hydrofluoric acid solutions by means of TBP.

The work described here consisted of two stages:

1. The choice of the optimum conditions for separating niobium and tantalum under static conditions; and checking the method developed by analyzing binary tantalum-niobium alloys.

2. Separating mixtures of niobium and tantalum in a continuous countercurrent extraction column.

The efficiency of separation was followed by means of the radioactive isotopes Nb^{95} and Ta^{182}.

The completeness of separation of a mixture of materials is determined by the difference in their partition coefficients K, which depend on the composition of the aqueous and organic phases, on temperature, etc.

In order to choose the best conditions for separating niobium and tantalum, a study was made of the effect of a number of factors on the extraction of the fluoride complexes of these elements with TBP (the work was carried out with synthetic solutions).

First of all, it was established how completely niobium and tantalum are extracted from a solution of hydrofluoric acid in the absence of salting out agents and other acids (in contrast to the extraction methods developed earlier for these elements), and in what way the concentration of the hydrofluoric acid in the original solution affects completeness of extraction.

As is evident from Fig. 1, tantalum passes more completely into the TBP phase at a considerably lower hydrofluoric acid concentration than niobium. This means that it is possible to separate the elements from 1 M HF when using only one extraction. About 90% of the tantalum is extracted by TBP, whereas almost all the niobum remains in the aqueous phase.

The presence of HCl or H_2SO_4 in the original solution essentially effects the partition coefficient of niobium. Thus, from 1 M HF-1 HCl, 35% niobium is extracted; while from 1 M HF-1 M H_2SO_4, 32.5% of the niobium is extracted. Thus, in order to ensure the most complete separation of niobium and tantalum, extraction should be carried out in the complete absence of HCl and H_2SO_4 in the aqueous phase.

Since the specific gravity of TBP is close to one, separation of the layers during extraction is too slow. In order to overcome this drawback it is usual to dilute the extractant with a lighter, inert organic solvent. For this purpose we used hydrogenated kerosene (a fraction boiling at 200-230°). In connection with the use of such a diluent, it was necessary to establish the extent to which TBP could be diluted without adversely affecting its extracting properties. The relation between the completeness of extraction of tantalum and the TBP concent of its mixture with kerosene is shown in Table 1.

TABLE 1

The Relation between Completeness of Extraction of Ta and TBP Concentration

TBP content, % by volume	Activity of the solution, impulses/min• ml		Ta extracted, %
	before extraction	after extraction	
10	103	104	0
20	103	52	50
40	103	15	86
80	103	6	94
100	103	4	96

It was found that diluting the TBP with kerosene so that the TBP content is 80% has little effect on the distribution of tantalum.

Increasing the temperature leads to a decrease in the partition coefficient of tantalum (Table 2). Accordingly, all subsequent experiments were carried out at room temperature.

On the basis of the experimental results obtained, the following parameters were chosen for the extraction separation of the fluoride complexes of Nb and Ta under static conditions: aqueous phase 1 M HF; extractant 80% TBP and 20% kerosene saturated with M HF; number of extractions 2; phase ratio 1 : 1; temperature 20°.

Initially, all the experiments were carried out with pure solutions containing niobium alone or tantalum alone. Subsequently, using the conditions chosen, the experiments were checked with mixtures of these elements, and it was found that the distribution hardly changed at all.

For analysis of binary tantalum-niobium alloys the following techniques were used. The alloy was oxidized in a muffle at 800-900° and an aliquot of the quinqueoxides (500 mg) fused with potassium pyrosulfate. The melt was leached with concentrated sulfuric acid. The hydroxides which were then precipitated from dilute solution were dried and subsequently dissolved in 1 M HF. Extraction was carried out twice (dissolution of the hydroxides in HF, and the extractions were carried out in a polyethylene vessel). After the layers had separated out, the niobium was determined in the aqueous phase while tantalum was determined in the combined organic phase (after reextraction of the tantalum with a 4% solution of ammonium oxalate + boric acid) by precipitation with phenylarsonic acid or ammonia after evaporation, till SO_3 fumes appeared, of the solution with H_2SO_4, and diluting with water. The precipitates were calcined to the quinqueoxide and weighed as such.

Table 3 contains results obtained during the determination of the tantalum content of alloys using the extraction method as well as other methods.

Some of the high results given by the extraction method can be explained by the partial transfer of niobium into the TBP phase (about 2-3%); this was confirmed by means of the radioactive indicator.

TABLE 2

The Relation between K_{Ta} and the Original Tantalum Concentration and the Temperature

t°	Original Ta concentration, mg/ml	X-ray spectrographic method		K_{Ta}	t°	Original Ta concentration mg/ml	X-ray spectrographic method		K_{Ta}
		tannin method	hypophosphite method				tannin method	hypophosphite method	
20°	0,1	925	Back ground	∞	50°	0,1	206	Background	∞
	0,5	1530	45	32,3		0,5	779	28	27
	2	4055	575	6,07		2	2958	468	4,3
	4	7653	4090	0.87		4	5555	4473	0,24

For work based on the method of continuous countercurrent extraction, a sectional packing column designed by N. I. Gel'perin was constructed from polyethylene. The total length of the column was 800 mm; the height of the packed section was 575 mm (5 sections); the internal diameter was 40 mm; the output was 0-200 ml/hr.

A schematic diagram of the operation of the setup is shown in Fig. 2; from vessels fitted on the wall, the solutions flowed under gravity into the column (extractant in the lower part, and the aqueous phase in the upper part of the column). In our experiments the ratio of the phases was kept at 1:1; the continuous phase consisted of 80% TBP and 20% kerosene. The phases were mixed in each of the sections by means of stirrers fitted on a shaft rotated by an electric motor at the rate of 250-300 rpm.

Separation of the layers in each section occurred in the packed zones consisting of spheres 2.5-3 mm in diameter. The extract was removed from the upper, and the raffinate from the lower connecting pipe of the column. The rate at which they were removed corresponded to the amount of reagents used up (about 200 ml/hr.).

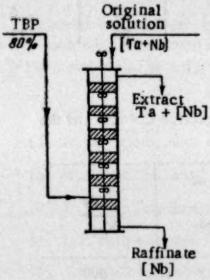

Fig. 2. Schematic diagram of the operation of the setup used for continuous and countercurrent extraction.

Using such a setup, extraction separation of synthetic mixtures of niobium and tantalum in various proportions was carried out. Distribution of the fluoride complexes of niobium and tantalum between the organic and aqueous phases under dynamic conditions differed from the distribution under static conditions. This made it necessary to study the relation between the completeness of extraction of the metal and the HF concentration of the original solution under conditions of continuous countercurrent extraction. As is evident from Table 4 satisfactory separation can be achieved by this method.

It is clear from Table 4 that in order to get niobium as free as possible from tantalum, extraction should be carried out from 1 M HF, since, in order to get the purest tantalum, it is best to work in less acid media.

The purity of the isolated products was checked by a spectral method (Table 5).

A sectional, packed column permits one to prepared, after only one passage through the column, niobium with a purity of 99.7-100%, for original ratios of Ta : Nb ranging from 1 : 5 to 5 : 1. The tantalum fraction is slightly contaminated with niobium (> 1%). Repeated extraction, after reextraction and conversion into the fluoride complex, permits more pure tantalum to be obtained.

On the basis of the experimental results, we have graphically calculated (see Fig. 3), the efficiency of a column during extraction of niobium and tantalum in 1 M HF using 80% TBP. It appears that the extraction of tantalum into the organic phase, under the given conditions, corresponds to four theoretical degrees of equilibrium, from which it follows that the height of the packed part of the column, corresponding to one degree of equilibrium is given by: $h_p = \frac{H}{n} = \frac{575}{4} = 144$ mm,

$$h_p = \frac{H}{n} = \frac{575}{4} = 144 \text{ mm},$$

where H is the over-all height of the packed layer and n is the number of theoretical plates.

TABLE 3

Determination of Tantalum in its Alloys with Niobium

Ta content, %	Ta found, %							Relative error of the extraction method, %
	x-ray spectrographic method	tannin method	hypophosphite method	chromatographic method	isotope dilution method	β-ray reflection method	Extraction method	
52	–	–	–	–	–	–	53	+ 1.9
32	–	–	–	–	–	–	37	+ 15.6
40	29	25	40.1	38	38	40	46	+15
42.5	–	48	41.6	42.1	–	42.5	46	+ 8.2
44	–	45	41.9	43.9	–	44	47	+ 6.8
50	52.5	45	48.3	46.3	–	–	50	0
23	–	–	–	–	–	–	26	+13

TABLE 4

Relation between the Completeness of Extraction of Nb and Ta on an Extraction Column and the Original HF Concentration

$[HF]_{original}$	Ta : Nb in the original solution	Extraction, %		$\frac{K_{Ta}}{K_{Nb}}$
		Ta	Nb	
0.1	1 : 1 (0.2 mg/ml each)	90	1	~900
0.25	1 : 1 (0.5 mg/ml each)	94	4	~392
0.5	1 : 1 (0.5 mg/ml each)	99	20	~396
0.5	1 : 5 (0.4 mg/ml; 2 mg/ml)	99	26	~283
0.5	5 : 1 (2 mg/ml : 0.4 mg/ml)	99	25	~300
1.0	1 : 1 (1 mg/ml each; 2 mg/ml each)	99-100	25	~300

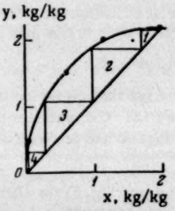

Fig. 3. Graphical determination of the number of theoretical degrees of equilibrium (1, 2, 3, 4) during extraction of tantalum in a sectionally packed column.,

The extraction method of separating niobium and tantalum using a sectionally packed column can be successfully applied both for analytical and technological purposes instead of long fractional methods.

SUMMARY

Using radioative indicators a study has been made of the effect of the concentration of hydrofluoric acid and tributylphosphate (TBP), temperature, hydrochloric and sulfuric acids, on the distribution of the fluoride complexes of niobium and tantalum between the aqueous phase and the TBP phase during extraction under static conditions.

A method has been developed for the extraction separation of niobium and tantalum which is applicable to the analysis of binary tantalum-niobium alloys.

TABLE 5

Spectrographic Characteristics of Nb_2O_5 and Ta_2O_5 after Their Separation on a Column

[HF]	Ta: Nb in the original sol.	Base	From which phase ppt is removed	Impurity, %
0,1	1 : 1	Nb_2O_5	Aqueous	0,05% Ta
		Ta_2O_5	Organic	>1% Nb
0,25	1 : 1	Nb_2O_5	Aqueous	0,07% Ta
		Ta_2O_5	Organic	>1% Nb
0,5	1 : 1	Nb_2O_5	Aqueous	0,1% Ta
		Ta_2O_5	Organic	>1% Nb
0,5	1 : 5	Nb_2O_5	Aqueous	0% Ta
		Ta_2O_5	Organic	>1% Nb
0,5	5 : 1	Nb_2O_5	Aqueous	0,3% Ta
		Ta_2O_5	Organic	>1% Nb
1,0	1 : 1	Nb_2O_5	Aqueous	0% Ta
		Ta_2O_5	Organic	>1% Nb

A continuous, sectionally packed extraction column has been used for the separation of mixtures of tantalum and niobium. It has been shown that under the conditions chosen (h_p of the packing = 144 mm) niobium of 99.7-100% purity can be obtained.

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THE SPECTROCHEMICAL DETERMINATION OF NIOBIUM IN ROCKS

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The determination of small amounts of niobium and tantalum in natural objects is a very interesting and pressing problem, which has not, as yet, found a satisfactory solution. The present article contains results of work on the determination of small amounts of niobium (up to 10^{-5}%) in rocks by a spectrochemical method. The first part of the work is devoted to a process for the chemical concentration of niobium, whereas the second is devoted to the clarification of a number of problems connected with developing a technique for spectrographic determination.

The sensitivity of the direct spectrographic determination of niobium amounts to 0.001% [1, 2]. For lower niobium contents, it is necessary to carry out preliminary chemical enrichment. Milner [3], during chemical enrichment of granites for determination of small amounts of niobium, used silicic acid and organic precipitants – tannin and cinchonine – as a collector. We used silicic acid, which proved very efficient both as a collector and as a carrier during the spectrographic determination of niobium after chemical enrichment. An aliquot of sample weighing about 1 g was decomposed with a mixture of hydrofluoric acid and sulfuric acid for complete removal of silicon dioxide. The residue was dissolved in dilute hydrochloric acid. To the hot solution obtained, at a pH 1, the following were added; a gel of silicic acid, a solution of gelatin, pyrogallol, and paper pulp. The precipitate was kept for two to three hours on a water bath, and then filtered after standing overnight. The precipitate was next calcined, ground, and analyzed spectrographically. Using this technique the bulk of the iron and aluminum were removed. Tantalum is precipitated together with niobium. The isolated precipitate of silicic acid also contains titanium, iron, and aluminum in amounts which do not interfere with the determination of niobium.

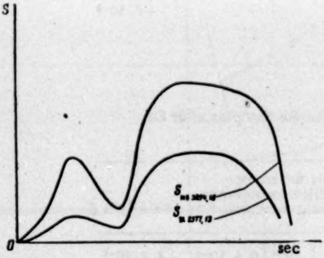

Fig. 1. Change in blackening of the lines of niobium (Nb 3094.18) and silicon (Si 2577.13) on evaporating a mixture of $SiO_2 + Nb_2O_5$ in a dc carbon arc.

The technique described for isolating and enriching niobium has been developed and checked on synthetic mixtures, which were similar in their chemical composition to the mean composition of rocks of the granite type. Niobium was introduced into the synthetic mixtures in the form of its oxalate complex. Completeness of precipitation from hydrochloric solutions containing iron, aluminum, titanium, calcium, and magnesium was checked by a radiochemical method.

In choosing the optimum conditions for the spectrographic determination of niobium, attention was given to the choice of the most sensitive analytical lines of niobium, to establishing the nature of the evaporation of micro amounts of niobium in a carbon arc in the presence of SiO_2, and to establishing the effect of titanium on the experimental accuracy.

As mentioned previously, according to the results of Rankama [1], and Ahrens [2], the sensitivity of niobium determination is 0.001% Nb_2O_5. They recommended the line Nb 4058.94 as the most sensitive line. For niobium

TABLE 1

A Spectrographic Determination of Niobium in Synthetic Mixtures after Enrichment

Sample wt.	Wt. of SiO_2 after enrichment, mg	Nb introduced		Nb found		Deviation, g
		g	%	g	%	
2	72,0	$8,9\cdot10^{-6}$	$4,4\cdot10^{-4}$	$7,8\cdot10^{-6}$	$3,9\cdot10^{-4}$	$-1\cdot10^{-6}$
2	49,3	$9\cdot10^{-6}$	$4,5\cdot10^{-4}$	$8\cdot10^{-6}$	$4,0\cdot10^{-4}$	$-1\cdot10^{-6}$
1	60,1	$1,2\cdot10^{-5}$	$1,2\cdot10^{-3}$	$1,3\cdot10^{-5}$	$1,3\cdot10^{-3}$	$+1\cdot10^{-6}$
1	55,9	$4\cdot10^{-6}$	$4\cdot10^{-4}$	$4\cdot10^{-6}$	$2\cdot10^{-4}$	0·0
1	49,1	$4\cdot10^{-6}$	$4\cdot10^{-4}$	$3,8\cdot10^{-6}$	$3,8\cdot10^{-4}$	$-2\cdot10^{-7}$
1	51,9	$1,2\cdot10^{-6}$	$1,2\cdot10^{-6}$	$1,1\cdot10^{-4}$	$1,1\cdot10^{-4}$	$-1\cdot10^{-7}$
1	67,7	$8,3\cdot10^{-7}$	$8,3\cdot10^{-5}$	$8,3\cdot10^{-7}$	$8,3\cdot10^{-5}$	0·0
1	52,1	$8,3\cdot10^{-7}$	$8,3\cdot10^{-5}$	$7,9\cdot10^{-7}$	$7,9\cdot10^{-5}$	$-4\cdot10^{-8}$

TABLE 2

A Spectrographic Determination of Niobium in Gneiss Samples after Enrichment (sample weight, 1 g)

Wt. of SiO_2 after enrichment, mg	Nb introduced, g	Nb found		Mean Nb content of the gneiss		Deviation, g
		g	%	g	%	
64,4	—	$5,3\cdot10^{-6}$	$5,3\cdot10^{-6}$	$5,5\cdot10^{-6}$	$5,5\cdot10^{-4}$	$-2\cdot10^{-7}$
33,7	—	$5,4\cdot10^{-6}$	$5,4\cdot10^{-4}$			$-1\cdot10^{-7}$
40,1	—	$5,8\cdot10^{-6}$	$5,8\cdot10^{-4}$			$+3\cdot10^{-7}$
43,2	$1,7\cdot10^{-6}$	$7,9\cdot10^{-6}$	$6,2\cdot10^{-4}$			$+7\cdot10^{-7}$
32,3	$1,7\cdot10^{-6}$	$7,8\cdot10^{-6}$	$6,1\cdot10^{-4}$			$+6\cdot10^{-7}$

TABLE 3

A Spectrographic Determination of Niobium in Biotite Granite Samples after Enrichment

Biotite granite	sample wt., g	Wt. of SiO_2 after enrichment, mg	Found		By the isotope dilution method*		Deviation, g
			g	%	g	%	
Fine grain	0,50	63,1	$4,4\cdot10^{-6}$	$8,8\cdot10^{-4}$	$3,2\cdot10^{-6}$	$6,4\cdot10^{-4}$	$+1,2\cdot10^{-6}$
Fine grain	0,50	58,8	$5,1\cdot10^{-6}$	$10,0\cdot10^{-4}$	$3,2\cdot10^{-6}$	$6,4\cdot10^{-4}$	$+1,9\cdot10^{-6}$
Average-sized grains	0,23	54,1	$5,8\cdot10^{-6}$	$2,5\cdot10^{-3}$	$6,4\cdot10^{-6}$	$2,8\cdot10^{-3}$	$-6,0\cdot10^{-7}$

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* Carried out by co-worker A. P. Savostin.

contents of 0.01* and higher, Ahrens suggested using the ultraviolet part of the niobium spectrum. Rusanov [4] gives different data on the sensitivity of the niobium lines – 4×10^{-3}% and 1×10^{-3}% for the lines Nb 2927.8 and Nb 3163.4, respectively, in the carbon arc.

Since the spectral sensitivity of a determination depends on many factors, in order to establish the absolute spectral sensitivity of the lines in the ultraviolet part of the niobium spectrum under the conditions we used, we carried out the following experiments. (We did not consider the line Nb 4058.94 which lies in the region of the continuous background of the molecular spectrum of the cyanide band).

Using a microburet, an oxalate solution of niobium was placed on the end of a carbon electrode, on which, beforehand, a few drops of polystyrene in benzene had been placed. The whole was then dried out and ignited in various excitation sources using various operational conditions. A qualitative evaluation of the niobium spectrum was made by means of a PS-18 spectroprojector. In order to exclude errors arising from impurities in the electrodes, the spectrum of an empty carbon electrode was photographed, under the niobium spectrum, with the same conditions present.

The absolute sensitivity of the niobium lines differs when they are excited in different sources. At niobium contents of 2×10^{-7} g, the niobium line is not observed when excitation is carried out in a ac arc (DG-1 generator) at a current strength of 13-14 amp, whereas in a dc arc at a current strength of 8-10 amp the following lines are weakly observed: (Nb II 3094, 18, Nb II 3163, 40; Nb II 3130.79.

On the basis of a limit of sensitivity of about 2×10^{-7} g Nb under our conditions, it is possible to make an approximate calculation of the minimum amount of sample required for an analysis. This assumption was confirmed by experimental results: the carrier – silicon dioxide – does not lower the sensitivity of niobium determination (the average amount of SiO_2 taken for an analysis amounted to 0.025 g) under conditions of complete ignition of the sample, and a minimum concentration of niobium of 9×10^{-4}%; the absolute amount was $2.5 \times 10^{-2} \cdot 9 \times 10^{-4}/100 = 2.25 \times 10^{-7}$ g Nb, i.e., this results agrees with the value found for the absolute spectral sensitivity of niobium.

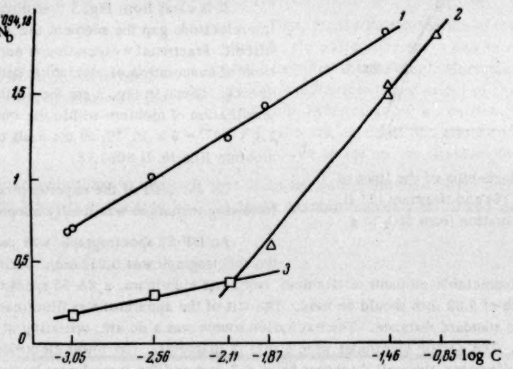

Fig. 2. Calibration curves for the determination of niobium on the basis of the absolute blackening of the line Nb 3094.18: 1) Using the spectrograph ISP-22; 2) using the KS-55 spectrograph for 0.14 to 0.008% niobium; 3) using the KS-55 spectrograph for 0.008 to 0.0009% niobium.

The base chosen for the determination of niobium was pure silicon dioxide which played the role of a carrier. Evaporation of silicon dioxide from the opening in a carbon electrode proceeds comparatively rapidly and uniformly; no fractionation is observed; the sensitivity of niobium determination under these conditions is fairly high; this also follows from the work of other authors [1, 4, 5]. The use of silicon dioxide as a carrier permits the use of the most sensitive line of niobium in the ultraviolet Nb 3094.18.

All the work was carried out on synthetically prepared mixtures; to an aliquot of SiO_2 slightly moistened with distilled water, was added, by means of a microburet, a standard oxalate solution of niobium; the solution was evaporated on a water bath and the residue calcined first on a sand bath, and then in a muffle. The powder obtained was carefully ground in an agate mortar.

A dc arc was used as the excitation source; this permits the sensitivity of the determination of niobium to be increased and the exposure time to be reduced.

In order to choose the method of evaporation (from the anode or from the cathode), a study was made of the distribution of the intensities of the silicon and niobium lines in the arc zone, along its length; photographs of the spectra were obtained by projecting a stigmatic image of the gas cloud on the spectrograph slit. As these photographs showed, the distribution of the intensities of the silicon and niobium lines changes with time; at the beginning of arc burning the lines are strengthened in the lower part of the spectrum; subsequently, the increase in intensity rapidly shifts along the length of the arc, whereas toward the end of arc burning, a significant increase is observed, independently of the method of evaporation, in the upper part of the spectrum. The total time for evaporation of silicon dioxide from the cathode is more than 3 minutes, and on evaporation from the anode, the total evaporation time is about 2 minutes. In order to determine the presence of niobium, we evaporated the test sample from the anode using a gap of 4 mm between the electrodes, diaphragming the ends of the electrodes in the process.

The shape and dimensions of the crater in the carbon electrode have an essential effect on the rate of evaporation of SiO_2. We consider that electrodes with very thin walls 0.3-0.5-mm thick are the most suitable. The sensitivity of the determination of niobium depends on the size of the sample. Accordingly, in our experiments we used not less than 20 mg.

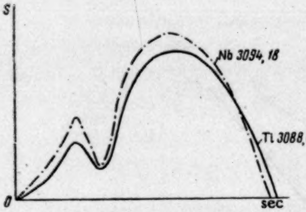

Fig. 3. Change in blackening of the lines of niobium (Nb II 3094.18) and titanium (Ti II 3088.03) during evaporation from SiO_2 in a dc carbon arc.

The changes in intensity of the niobium and silicon lines with time are shown in the evaporation curves (Fig. 1).

It is clear from Fig. 1 that niobium passes into the interelectrode gap the moment the arc is struck, as does the silicon. Fractional evaporation is not observed. The total time of evaporation of niobium is determined by the amount of SiO_2. Given in Fig. 2 are the calibration curves for the determination of niobium within the concentration limits $1.4 \times 10^{-1} - 9 \times 10^{-4}\%$ on the basis of the blackening of the niobium line Nb II 3094.18.

On the basis of the experimental results obtained, the following technique was finally adopted.

An ISP-22 spectrograph was used; the slit width of the spectrograph was 0.012 mm. During analysis of enriched samples containing appreciable amounts of titanium, iron, and aluminum, a KS-55 spectrograph with quartz optics and a slit width of 0.02 mm should be used. The slit of the apparatus was illuminated with a three-lens condenser system at a standard distance. The excitation source was a dc arc, operating at a voltage of 220 v and current of 9-10 amp. The carbon electrodes were 6 mm in diameter. The lower electrode had a crater 8-9 mm deep and 3.5 mm in diameter, the wall thickness being 0.3 mm and the interelectrode distance was 4 mm. The ends of the electrodes were diaphragmed and the duration of preliminary ignition was 20 sec. Photographs were taken for 90-100 sec right up to complete burning of the sample. The photographic plates used were type I, sensitivity 4 GOST units (spectrograph ISP-22) or spectrographic type II, sensitivity 16 GOST units (spectrograph KS-55). Determination was made on the basis of the absolute blackening of the niobium line NB II 3094.18. Standards were prepared by adding a niobium solution to chemically pure SiO_2. The mixtures obtained were evaporated, calcined, and ground.

Using this technique, synthetic mixtures of the granite type, a natural sample of gneiss and samples of biotite granites were analyzed, after chemical enrichment by the method described above. The results are given in Tables 1-3. In order to check the results the method of additions was also used.

The niobium content of the gneiss was determined as the mean of five parallel determinations; the mean square experimental error was ± 8%.

For determination of niobium on the basis of the absolute blackening, the mean square error of a single determination was about ± 20%.

The error of a single determination of microamounts of niobium in samples is made up from errors arising from the chemical operations during concentration, and from the errors of the spectrographic method.

Results for the determination of niobium the synthetic mixtures, gneiss samples, and in granites can be regarded as quite satisfactory.

When the test sample does not contain titanium [6], niobium can be conveniently determined on the basis of relative blackening using titanium in amounts of 1-5 × 10^{-2}% as an internal standard. In such cases, titanium is added to both the standards and the samples as a standard solution, with subsequent drying and calcining of the silicon dioxide.

In Fig. 3 are shown the curves illustrating the change in absolute blackening of the lines Nb II 3094.18 (excitation potential equal to 4.52 ev) and Ti 3088.03 (excitation potential equal to 4.07 ev) as a function of the evaporation time. Similar evaporation curves are obtained when the current is altered.

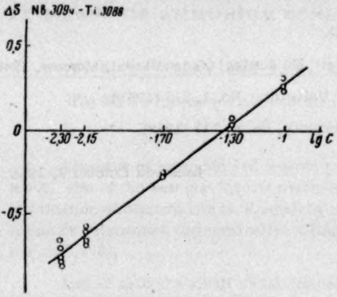

Fig. 4. Calibration curve for the determination of niobium on the basis of relative blackening.

A calibration curve plotted within the coordinates relative blackening – logarithm of the concentration – is shown in Fig. 4.

On using titanium as an internal standard, the mean square error of a determination for a niobium concentration of 5 × 10^{-2}% amounts to ± 6.4%, whereas for lower concentrations, it is approximately ± 20% (for 2.3 × 10^{-3}% Nb, it is ± 17%).

Thus, for the determination of the order of 10^{-3}% of niobium, the calibration curve can be constructed on the basis of absolute blackening. Since there are a number of published references to the effect of titanium on the accuracy of niobium determination, we carried out some experiments to establish the extent of this effect on the intensity of the line Nb 3094.18 for various titanium contents (Fig. 5).

The results obtained permit one to conclude that under the conditions used in the suggested method, titanium has no effect on the intensity of the line Nb 3094.18 for titanium contents of 1% and less in the ignited sample.

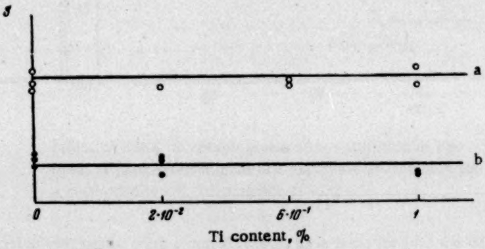

Fig. 5. Relation of the blackening of the line Nb 3094.18 for a) 0.25% and b) 0.002% of niobium in the standard.

In conclusion, the authors wish to thank I. P. Alimarin for his continued interest in the work and for his valuable advice.

SUMMARY

A technique has been suggested for the chemical enrichment of niobium, which is based on its coprecipitation with silicic acid in the presence of gelatin and pyrogallol; this technique has been treated experimentally;

a spectrographic method has also been developed for the determination of 0.1-0.0009% of niobium in the isolated silicic acid using Russian apparatus.

Determination of niobium in gneiss and granite is possible at niobium contents of up to $n \times 10^{-5}\%$ with an error of about 20%.

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GRAVIMETRIC AND TITRIMETRIC METHODS OF DETERMINING BISMUTH BY MEANS OF AMMONIUM BENZENE- AND NAPHTHALENESELENINATES

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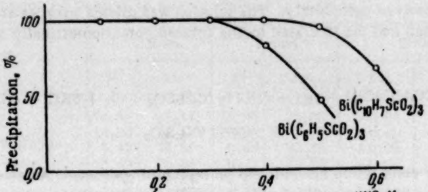
A number of inorganic and organic precipitating agents are used for the gravimetric determination of bismuth. One of the best gravimetric methods is based on the precipitation of bismuth with selenious acid [1-5]. Determination of bismuth can be finished by weighing it, (after drying the precipitate at 110-120°) as $Bi_2(SeO_3)_3$, or it can be determined titrimetrically. Orthophosphoric acid and alkali metal phosphates have also been recommended [6-8].

Arsenic acid and alkali metal arsenates form compounds with bismuth which are sparingly soluble in water and which are reminiscent of phosphates [9-10]. Methods for the gravimetric and titrimetric determination of bismuth and for its separation as the arsenate have not been studied very much and are of no great practical importance, being inferior to the phosphate and other methods [11, 12]. Of organic reagents, phenylarsonic acid, cupferron, 8-hydroxyquinoline, gallic acid, pyrogallol, etc. have been used for the determination of bismuth [1].



Effect of HNO_3 on completeness of precipitation of bismuth as benzeneseleninate and naphthaleneseleninate for a concentration of the reagents of 2.3%.

We should like to suggest two new reagents for the gravimetric and titrimetric determination of bismuth. These compounds are $C_6H_5SeO_2NH_4$ and $C_{10}H_7SeO_2NH_4$ and they permit the determination of bismuth in the presence of many elements: Ag, Be, Ca, Al, Zn, Mn, Ni, Co, Cd, Cu, Pb, etc. [13].

The reagents $C_6H_5SeO_2NH_4$ and $C_{10}H_7SeO_2NH_4$ precipitate bismuth from mineral acid solutions as crystalline precipitates which are soluble in concentrated acids, and are also decomposed by alkalis. The limiting dilution for bismuth benzeneseleninate is 1 : 400,000, and for the naphthaleneseleninate it is 1 : 650,000. The chemical composition of the precipitates dried at 110° corresponds to the formula $Bi(R\text{-}SeO_2)_3$ where R is C_6H_5 or $C_{10}H_7$. Bismuth can be determined by weighing as $Bi(R\text{-}SeO_2)_3$ after drying the precipitate at 110-120°, or it can be determined iodometrically.

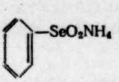
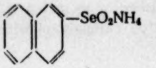
In order to investigate the effect of the concentration of HNO_3 on the completeness of precipitation of bismuth as $Bi(R\text{-}SeO_2)_3$, various amounts of mineral acid were added, and the solution diluted to 100 ml. The final solution was then heated to 70-80° and bismuth precipitated with either $C_6H_5SeO_2NH_4$ or $C_{10}H_7SeO_2NH_4$. The precipitate was washed, calcined, and then weighed as Bi_2O_3. The results obtained are given in the diagram.

During the gravimetric determination of bismuth, after precipitation of the bismuth the precipitate plus solution was heated on an electric hotplate for 25-30 minutes, and then, after cooling the solution, the precipitate was filtered off on a No. 4 crucible (with a porous bottom); it was washed carefully with distilled water, dried at 110-120°, and weighed as $Bi(R\text{-}SeO_2)_3$.

The results obtained are given in Table 1.

TABLE 1

A Determination of Bismuth as Benzene- and Naphthaleneseleninates (in mg)

Regeant	Bi taken	Bi found	Error	Reagent	Bi taken	Bi found	Error
	11,26	11,25	—0,01		11,26	11,27	+0,01
	11,26	11,27	+0,01		11,26	11,25	—0,01
	5,63	5,63	±0,00		5,63	5,62	—0,01
	5,63	5,61	—0,02		5,63	5,63	±0,00

For the titrimetric determination of bismuth, the precipitate of the benzeneseleninate was dissolved in hydrochloric acid and the benzeneseleninic acid was titrated iodometrically, potentiometrically, or amperometrically, using a rotating platinum microelectrode. The precipitate, after precipitation of bismuth with benzeneseleninic acid, was filtered off, carefully washed with distilled water, and washed into the beaker to be used for titration. Some hydrochloric acid was then added; this was followed by 0.5-1.0 g of tartaric acid, and the solution heated until the precipitate had dissolved completely. The solution was diluted with water. A two-to threefold excess of potassium iodide was added and the liberated iodine titrated potentiometrically or amperometrically with sodium thiosulfate:

$$2C_6H_5SeO_2H + 6KI + 6HCl = (C_6H_5Se)_2 + 3I_2 + 6KCl + 4H_2O \qquad (1)$$

$$Bi \equiv 9I \equiv 9Na_2S_2O_3$$

At the same time, for comparison bismuth was precipitated with selenious acid by the method described in the literature [2]. The precipitate was washed with water, dissolved in nitric acid, and tartaric acid added; the liberated iodine was again titrated with sodium thiosulfate:

$$H_2SeO_3 + 4KI + 4HCl = Se + 2I_2 + 4KCl + 3H_2O \ldots \qquad (2)$$

$$Bi \equiv 6I \equiv 6Na_2S_2O_3$$

The results obtained are given in Tables 2 and 3.

It should be pointed out that the potentiometric and amperometric methods of determining bismuth by means of selenious acid have some essential drawbacks, namely: reduction of selenious acid by potassium iodide proceeds to elemental selenium, which is deposited on the platinum electrode and the latter accordingly ceases to react to changes in potential difference. This interferes with establishment of the equivalence point. Accordingly, potentiometric titration of large amounts of H_2SeO_3 is very difficult, and amperometric titration, even of only small amounts of H_2SeO_3, is impossible in practice. Table 2 and Table 3 contain the best of many results obtained during potentiometric and amperometric determination of bismuth by means of selenious acid.

Reduction of $C_6H_5SeO_2H$ with potassium iodide proceeds to diphenylselenide which does not affect the accuracy of establishing the equivalence point when either the potentiometric or amperometric methods are used.

TABLE 2

A Potentiometric Determination of Bismuth

Compound	Bi taken, mg	$Na_2S_2O_3$ N/40, ml	Bi found, mg	Error, mg	Compound	Bi taken, mg	Na_2SO_3 N/40, ml	Bi found, mg	Error, mg
$Bi_2(SeO_3)_3$	8,45	9,68	8,49	+0,04	$Bi(C_6H_5SeO_2)_3$	16,90	28,95	16,92	+0,02
	8,45	9,60	8,42	—0,03		16,90	28,97	16,93	+0,03
	4,23	4,89	4,28	+0,05		8,45	14,45	8,44	—0,01
	4,23	4,74	4,20	—0,03		8,45	14,45	8,45	±0,00
						4,23	7,23	4,23	+0,00
						4,23	7,24	4,24	+0,01

TABLE 3

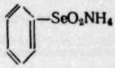
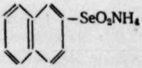
Amperometric Determination of Bismuth

Compound	Bi taken, mg	$Na_2S_2O_3$ N/40, ml	Bi found, mg	Error, mg	Compound	Bi taken, mg	$Na_2S_2O_3$ N/40, ml	Bi found, mg	Error, mg
$Bi_2(SeO_3)_3$	4,23	4,85	4,26	+0,03	$Bi(C_6H_5SeO_2)_3$	4,23	7,23	4,23	+0,00
	4,23	4,78	4,20	—0,03		4,23	7,25	4,24	+0,01
	2,12	2,33	2,09	—0,03		2,12	3,59	2,10	—0,02
	2,12	2,46	2,16	+0,04		2,12	3,64	2,13	+0,01

Lead, at a pH of not less than 4, is precipitated with ammonium benzene- or napthaleneseleninate, but the coarse crystalline precipitate dissolves readily in dilute nitric acid. Bismuth, on the other hand, is quantitatively precipitated by these reagents from fairly acid solutions. On this basis we have studied the possibility of determining bismuth quantitatively in the presence of lead. The lead content of the filtrate remaining after removal of the bismuth was determined by precipitation with thiourea, with subsequent conversion of the lead into $PbCrO_4$. Determination of lead was finished iodometrically [14].

TABLE 4

A Determination of Bismuth in the presence of Lead (in mg)

Reagent	Taken		Found		Error	
	Bi	Pb	Bi	Pb	Bi	Pb
	16,90	25,11	16,89	25,05	—0,01	—0,06
	16,90	25,11	16,92	—	+0,02	—
	8,45	75,33	8,48	75,35	+0,03	+0,02
	8,45	75,33	8,43	75,25	—0,02	—0,08
	5,63	150,66*	5,61	—	—0,02	—
	5,63	150,66*	5,64	150,60	+0,01	—0,06
	16,90	25,11	16,88	—	—0,02	—
	16,90	25,11	16,89	—	—0,01	—
	8,45	75,33	8,43	75,37	—0,02	+0,04
	8,45	75,33	8,48	75,24	+0,03	—0,09
	5,63	150,66*	5,65	—	+0,02	—
	5,63	150,66*	5,60	150,58	—0,03	—0,08

* Bismuth was determined after reprecipitation.

As is evident from the results given in Table 4, when the amount of lead present is not more than 10% of that of bismuth, then the former does not affect the accuracy of the determination of bismuth by the benzene- or napthaleneseleninate method. At higher lead contents the bismuth must be reprecipitated.

SUMMARY

Two new reagents — $C_6H_5SeO_2NH_4$ and $C_{10}H_7SeO_2NH_4$ — are suggested for the gravimetric determination of bismuth; in mineral acid solutions these reagents form white crystalline precipitates with bismuth.

The composition of the precipitates corresponds to the formulas $Bi(C_6H_5SeO_2)_3$ and $Be(C_{10}H_7SeO_2)_3$. Bismuth can be determined by weighing it in the form of its benzene- or naphthalenseleninate after drying the precipitates at a temperature of 110-120°.

It has been shown that it is possible to determine bismuth titrimetrically by dissolving bismuth benzeneseleninate in a mixture of mineral acid and tartaric acid, and then iodometrically titrating the benzeneseleninic acid by a potentiometric or amperometric method. The relative error for determination of 5 to 20 mg of Bi does not exceed 0.5%.

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THE ANALYTICAL APPLICATION OF 8-MERCAPTOQUINOLINE (THIOOXINE) AND ITS DERIVATIVES

COMMUNICATION 8. A NEW PHOTOMETRIC METHOD FOR THE DETERMINATION OF RHENIUM IN THE PRESENCE OF MOLYBDENUM, TUNGSTEN, AND OTHER ELEMENTS*

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The rhenium content of minerals lies within the limits of 10^{-6}-10^{-8}% and lower [1]. As a result of this, analytical methods are required which will permit determination of low concentrations of rhenium against a background of molybdenum and a number of other elements which usually accompany rhenium. Despite the considerable amount of work carried out by research workers on rhenium, and despite the wide possibilities opened up by the existence of rhenium in various valence states, the analytical chemistry of rhenium has not been developed sufficiently, and, to a considerable extent, does not satisfy modern demands. This is true in particular of the determination of rhenium in the presence of appreciable overwhelming amounts of molybdenum, tungsten, and other elements.

While we do not wish to enumerate all the published methods for the determination of rhenium, we shall briefly discuss the present position with regard to the analytical determination of rhenium.

The x-ray spectrographic method first applied by V. and I. Noddak [3] for the determination of rhenium continues to be the subject of study for a number of research workers [4], but this method has not yet achieved the accuracy of chemical methods, and, because of its low sensitivity, cannot be used for the direct determination of rhenium in natural objects without preliminary concentration.

Spectrographic methods of determining rhenium are not sensitive enough; suppression of the intensity of the spectral lines of rhenium by accompanying elements has been observed [5, 6].

Gravimetric methods demand preliminary determination of a number of elements, and, for a variety of reasons, have not found application for the determination of gamma amounts of rhenium [7-12].

In 1932, Geilmann, Wrigge, and Weibke [13] suggested a photometric method for the determination of rhenium in the form of its compound with thiocyanate (after reduction of $HReO_4$ with stannous chloride), to which the composition $ReO(SCN)_4$ has been ascribed. But, as Ryabchikov and Lazarev [14] have shown, the colored compound is the salt $K_3[ReO_2(SCN)_4]$ or $K[ReO(SCN)_4]$. This is the method that has found the widest application, and is suitable for the determination of 0.5 to 500 γ of Re according to one source [5], and for the determination of 63 to 5000 γ Re according to another [15]. The thiocyanate method requires the preliminary separation of molybdenum, tungsten, niobium, and a number of other elements. Anisomov [16] has found that the color given by the thiocyanate complex of molybdenum can be eliminated by means of hydroxylamine hydrochloride.

On this principle a method has been suggested for the qualitative detection of rhenium at a limiting concentration of 1 : 66,000 at a ratio of Re : Mo = 1 : 3700.

Poluéktov [17] has suggested a very sensitive photometric method for the determination of 0.001-0.1 γ Re in 1.5 ml of solution. The method is based on the catalytic acceleration by perrhenates of the reduction of tellurates by stannous chloride. Only small amounts of molybdenum are permissible.

In 1939, Willard and Smith [12] suggested tetraphenylarsonium chloride for precipitating perrhenates. Later tetraphenylarsonium chloride was studied in more detail and was used for the photometric determination of rhenium in the far ultraviolet, and also for preliminary separation of rhenium, and its subsequent determination as the thiocyanate complex [18, 19]. By means of this reagent it is possible to determine rhenium in the presence of 20 mg Mo and W, and also to separate rhenium from molybdenite, with subsequent photometric determination by the thiocyanate method [18]. Unfortunately, a number of elements: Hg, Bi, Pb, Ag, Sn, VO^{2+} and some anions (fluorides, bromides, iodides, thiocyanates, etc.) interfere with determination of Re by this very promising reagent. Presumably, more detailed work would show that the number of elements which can interfere is even greater (e. g., the platinum metals).

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* For communication 7, see J. Anal. Chem. 14, 523 (1959).

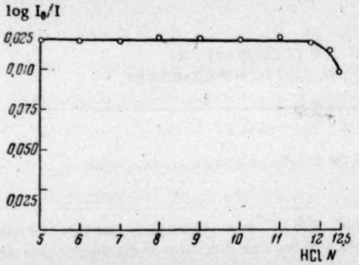

Fig. 1. The relation between the light absorption of chloroform extracts of rhenium thiooxinate and the hydrochloric acid concentration of the solution (30 γ Re taken; measurements carried out on a FÉK-M apparatus; blue filter, cuvette 1 cm).

Another method which has been suggested is reduction of perrhenic acid with hydrazine [20], or with a divalent chromium salt [21], and then carrying out a photometric determination of the solution of hexachlororrhenic acid H_2ReCl_6 at 281.5 mμ. The specificity of the method is apparently low.

Research workers have also devoted their attention to a study of the interactions of the lower valence states of rhenium with dioximes. The first article on the reaction of rhenium with dimethylglyoxime was that of Tugarinov [22]. This was followed by: Tribildt's article [23] on the reaction of Re with α-furildioxime, the article by Peshkova and Gromova [24] on the reaction of rhenium with dioximes as a function of the structure of the reagents, and the article of Fischer and Meloche [25] on the reaction of rhenium with α-benzyldioxime. Since dioximes only react with the lower valence states of rhenium (4 or 5 valence), the reactions are carried out in the presence of stannous chloride. Mo, W, and some platinum metals interfere with determination of rhenium by means of dioximes.

TABLE 1

Determination of Re in Pure Solutions

Re taken, γ	Re found, γ	Error, %	Re taken, γ	Re found, γ	Error, %
5	5.3	+6	50	50	0
10	10.2	+2	100	99	−1
20	19.5	−2.5	200	206	+3

Geilman and Rolf Neeb [26] have suggested 2,4-diphenylthiosemicarbazide as a reagent for rhenium. The reagent gives a color reaction (the red-colored compound can be extracted with chloroform) directly with the perrhenate ion without preliminary reduction. It is possible that the reagent itself functions as a reducing agent as well. 2,4-Diphenylthiosemicarbazide permits determination of Re in the presence of only small amounts of molybdenum.

Chernikhov and Dobkina [27] have established that perrhenate ions form a white-yellow precipitate with sodium diethyldithiocarbamate in concentrated hydrochloric acid. No indications are given in their article of the possibility of separating or determining rhenium with diethyldithiocarbamate in the presence of foreign elements.

Titrimetric methods are only used for the determination of large amounts of rhenium, preferably in pure solutions.

Electrolytic [28, 29] and polarographic [30, 31, 32] methods, despite the fairly high sensitivity of the latter, have not yet found application for the determination of small amounts of rhenium in natural objects.

It has been shown earlier [35] that thiooxine forms exceptionally stable inner-complex salts with a number of elements, these salts being intensely colored and readily soluble in organic solvents.

Both acid and alkali solutions of potassium perrhenate also react with thiooxine to form differently colored, in all probability, inner-complex salts, which are insoluble in water but are readily extracted with chloroform, and extracted somewhat less readily by other organic solvents. A photometric method for the determination of small amounts of rhenium by means of thiooxine is described below.

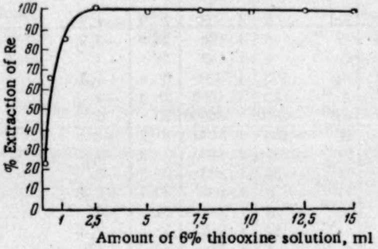

Fig. 2. Curve for the extraction of rhenium from 10 N hydrochloric acid as a function of the amount of 6% thiooxine solution; final volume, 50 ml.

The Interaction of Rhenium with Thiooxine in Various Media. Thiooxine hydrochloride $C_9H_6NSH \cdot HCl$ was used in the work described here [33, 34]. On mixing a solution of potassium perrhenate with a 1% alcoholic solution of thiooxine hydrochloride, thiooxinates corresponding to the various valence states of rhenium are formed. In acid solutions, a brown or yellow-brown amorphous precipitate is formed. Upon heating in alkali solutions, a light brown precipitate is formed.

The completeness of the reaction depends on the time (usually 20-30 minutes), on the excess of thiooxine, and on the nature of the acid. Perrhenate does not react completely in sulfuric acid solutions, whereas in hydrobromic acid solutions the reaction proceeds rapidly. However it is not reproducible to the degree desired, presumably because the hydrobromic acid reduces the perrhenate ion to the lower valence states [2] in which less intensely colored complexes are formed with thiooxine. Completely stable colored-compounds are obtained in hydrochloric acid solutions. Heating the solution in a boiling water bath for 2-3 minutes leads to completion of the reaction.

We first studied the extractability of the compounds formed as a function of the acid concentration.

Amounts of 50 γ lots of Re in the form of a solution were introduced into 200 ml Erlenmeyer flasks followed by various amounts of concentrated hydrochloric acid to give final solutions of a known normality. Water was added to bring the volume up to 50 ml together with 5 ml of 6% solution of thiooxine in hydrochloric acid of the same normality. The flasks were placed in a boiling water bath for 3 minutes. They were then rapidly cooled under the tap, and the contents transferred to a 150-200 ml separating funnel. By shaking thoroughly for 3-4 minutes with 10 ml of chloroform, the rhenium thiooxinate was extracted. After filtering the yellow chloroform extracts through a plug of cotton wool, the solutions were measured photometrically in a 1 cm cuvette on a SF-4 spectrophotometer at 438 mμ. As is evident from Fig. 1, rhenium thiooxinate is stable and is extracted from media whose normality varies from 5-11.75 N HCl. We did not study the reaction in solutions with a lower concentration than 5 N of HCl.

Thus, rhenium thiooxinate is formed in a wide range of acid concentration, Accordingly, there is no need to keep to a definite acidity very strictly. The higher the hydrochloric acid concentration, the smaller the number of elements which react with thiooxine, and, accordingly, the more selective the reaction for rhenium. In such strongly acid solutions as 8-11 N, very few elements react with thiooxine (some platinum metals). The best extractant for the rhenium thiooxinate formed under these conditions is chloroform.

In order to ensure that the reaction proceeds quantitatively in a medium of 10 N HCl an excess of reagent is necessary. As is evident from Fig. 2, for complete extraction of rhenium from 10 N HCl, not less than 2.5 ml of a 6 % solution of thiooxine in a volume of 50 ml is required. Larger amounts of thiooxine do not affect the color intensity of the chloroform extracts.

TABLE 2

A Determination of Re in the Presence of Foreign Elements

Re taken, γ	Foreign element, mg	Re : Me	Re found, γ	Error, %	Re taken, γ	Foreign element, mg	Re : Me	Re found, γ	Error, %
20	$\mathrm{Mo^{VI*}}$ — 100	1 : 5000	19	−5	30	$\mathrm{Sn^{II*}}$ — 5	1 : 166	29,8	−0,7
100	» — 100	1 : 1000	97	−3	30	$\mathrm{Sn^{IV*}}$ — 50	1 : 1666	31	+3
20	$\mathrm{W^{VI*}}$ — 10	1 : 500	20	0					
100	» — 10	1 : 100	95	−5	30	$\mathrm{Se^{IV*}}$ — 4	1 : 133	28,9	−4,7
20	$\mathrm{Fe^{III*}}$ — 25	1 : 1250	21	+5	30	$\mathrm{Te^{IV*}}$ — 5	1 : 166	28,9	−3,7
20	Ni — 200	1 : 10000	21	+5	30	$\mathrm{Cu^{II*}}$ — 4	1 : 133	31	+3
20	Co — 250	1 : 12500	19,5	−2,5	30	Ag —100	1 : 3300	30,4	+1,3
30	Zn — 100	1 : 3300	29	−3	30	$\mathrm{Au^{III}}$ — 50	1 : 1660	28,8	−4
30	Cd — 125	1 : 4166	28,2	−6	30	$\mathrm{Mn^{II}}$ —2000	1 : 66600	30	0
30	$\mathrm{V^{V}}$ — 25	1 : 833	29	−3	30	$\mathrm{U^{VI}}$ —100	1 : 3300	31,2	+4
30	In — 50	1 : 1666	30	0	30	$\mathrm{Pb^{II}}$ —250	1 : 8330	29,9	−0,3
30	$\mathrm{Hg^{II}}$ — 25	1 : 833	31	+3	30	$\mathrm{Tl^{I*}}$ — 25	1 : 833	28,5	−5
30	$\mathrm{Sb^{III}}$ — 10	1 : 333	32	+7	30	$\mathrm{Tl^{III*}}$ — 5	1 : 166	30,7	+2,3
30	$\mathrm{Ru^{III*}}$ — 1	1 : 33	32	+7	30	$\mathrm{Ge^{IV}}$ — 10	1 : 333	32	+7
30	$\mathrm{Pt^{IV*}}$ —0,7	1 : 23	29	−3	30	$\mathrm{As^{V*}}$ — 17	1 : 566	32,2	+7,3
30	$\mathrm{Os^{VIII}}$ —0,15	1 : 5	32	+7	30	$\mathrm{As^{III*}}$ — 1	1 : 33	44	+47
30	$\mathrm{Ir^{IV*}}$ — 10	1 : 333	28,7	−4	30	$\mathrm{Bi^{III*}}$ — 60	1 : 2000	29	−3
30	$\mathrm{Rh^{III*}}$ — 2	1 : 66	31	+3	30	$\mathrm{Ce^{III}}$ —500	1 : 16600	31,3	+3,4
30	$\mathrm{Nb^{V}}$ — 5	1 : 166	28	−6,7	30	$\mathrm{Cr^{III}}$ —500	1 : 16600	30	0
30	$\mathrm{Ta^{V}}$ — 20	1 : 666	30,5	+1,6	30	Al — 500	1 : 16600	30,2	+0,7
30	$\mathrm{Ti^{IV}}$ — 50	1 : 1666	29,5	−1,7	30	Zr — 500	1 : 16600	29,2	−2,7

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* The values given for the elements marked with asterisks in the table are the limiting permissible values for those elements (in the absence of other elements in the 50 ml of the test solution). The limiting permissible amounts of the other elements have not been studied.

Absorption Spectrum of Rhenium Thiooxinate and Conformity to Beer's Law. The absorption spectrum of rhenium thiooxinate was taken on a SF-4 spectrophotometer. The chloroform extracts were prepared in the same way as that described in the analytical procedure (see below). In Fig. 3 are given absorption curves for three different concentrations of rhenium thiooxinate. The absorption maximum of the complex is located at 438 mμ, and the mean value of the molar extinction coefficient is 8470.

A study of the conformity of the chloroform extracts of rhenium thiooxinate to Beer's Law, and the determination of rhenium in pure solutions was carried out as described below: the extinction of the extracts was measured at 438 mμ in a 1 cm cuvette. As is evident from Fig. 4, the calibration curve constructed for the limits 1 to 40 γ Re in 1 ml of $CHCl_3$ (5-200 γ of Re in the solution being analyzed), deviates only slightly from linearity. By using a 0.5 cm cuvette, it is possible to determine even more than 200 γ Re. By working with a 1 cm cuvette and carrying out the extraction with 5 ml of chloroform, completely satisfactory results can be obtained during determination of 5 γ Re, and apparently, smaller amounts can be determined.

Results for the determination of Re in pure solutions are given in Table 1.

Determination of Rhenium in the Presence of Foreign Elements. Thiooxine, as a reagent of the R-SH type, in complete agreement with the views developed by V. I. Kuznetsov [36], interacts in aqueous solutions only with elements which form sulfides which are stable in the presence of water. Accordingly, particular attention was given to a study of the effect of these elements on the accuracy of rhenium determination.

TABLE 3

The Effect of Anions on the Accuracy of Re Determination (30 γ Re taken each time)

Foreign anion, mg	Re found, γ	Error, %	Foreign anion, mg	Re found, γ	Error, %
Bromide – 1500	29	−3.4	Perchlorate – 500	27.9	− 7
Iodide – 1000	28	−6.7	Tartrate – 2000	30	0
Fluoride – 1000	32	+6.6	Arsenate – 175	0	−100
Sulfate – 2000	30	0	Arsenate – 17	32.5	+ 6.3
Phosphate – 2000	30.5	+1.7	Hypophosphite – 500	12	− 60
Borate – 1000	31.5	+5	Hypophosphite – 5	31	+ 3.3
Acetate – 2000	29.6	−1.3	Arsenite – 1	44	+ 47
Oxalate – 1000	28	−6.7	Nitrate – 100	0	−100

The fact that rhenium thiooxinate in the presence of excess thiooxine, can be extracted in a medium of 5-11.75 N hydrochloric acid (Fig. 1) means that it is possible to vary the conditions for determining rhenium widely with the object of removing interference on the part of many elements. In strongly acid solutions (2-6 N HCl) only a few elements react with thiooxine: Hg, Ag, Au, Cu, Mo, W, Pt, Pd, Ru, and Os. At higher acidities (8-10 N HCl) Hg, Ag, Cu, Mo, and W cease to react with thiooxine. Accordingly, rhenium should be determined in 9-10 N hydrochloric acid.

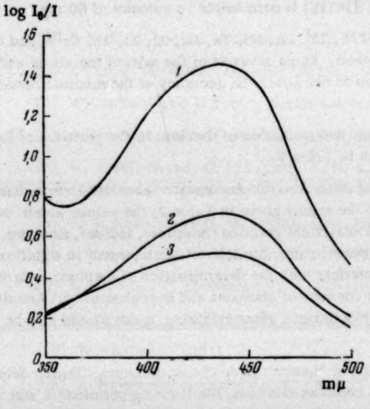

Fig. 3. Absorption spectrum of rhenium thiooxinate in chloroform obtained in a medium of 10 N HCl; λ_{max} = 438 mμ. 1) 0.00016 M solution; 2) 0.00008 M solution; 3) 0.000053 M solution, cuvette 1 cm.

Molybdenum and tungsten in amounts of 100 and 10 mg respectively do not interfere with the determination of rhenium when the technique described below is used. In the presence of large amounts of Mo and W, low results are obtained for Re because of the complexing of thiooxine by these elements. In the presence of large amounts of other foreign elements the limiting permissible amounts of Mo and W decrease because of additional complexing of thiooxine by these elements.

Iron present in considerably larger amounts than rhenium sometimes partially passes into the extract and leads to high results for Re. Masking of iron by fluorides or phosphates in a medium of 10 N HCl is not possible. Interference from iron was avoided by a double extraction as described in the analytical procedure. During this procedure it was also established that in order to free the extract from drops of water, it is necessary to dry it with 1-2 granules of anhydrous $CaCl_2$, but not to filter it through cotton wool. Using such a method, 25 mg of iron does not interfere with determination of rhenium.

Quinquevalent arsenic is permissible to the extent of 17 mg. Large amounts which are reduced to the elemental state trap rhenium.

Platinum metals, in view of the high stability of their thiooxinates are only permissible in small amounts: Pt-0.7 mg, Ru-1 mg, Os-0.15 mg. Rh does not interfere in amounts up to 2 mg (larger amounts were not studied), Ir-10 mg; Pd should be absent.

Gold which, is precipitated from 10 N HCl in the form of its very stable thiooxinate, coprecipitates rhenium thiooxinate. Nevertheless, rhenium can still be determined in the presence of large amounts of Au (e. g., 50 mg)

TABLE 4

Determination of Re in Synthetic Mixtures

Re taken, γ	Foreign elements, mg	Re found, γ	Error, %
30	Mo-50, Fe-20, Cu 2, W-2, Pb-50, Ni-15, Co-15, Cd-10, U-10, Mn-10	30	0
30	Mo-30, Fe-15, Zn-20, Mn-100, Cr-50, Hg-10, V-5, Ti-25, Ag-20, In-10, Zr-50, As^V-5, W-2, Ta-10	29	-3

when the following technique is used. After the test solution has been heated for 3 minutes in a boiling water bath and then cooled, 5-7 ml of a saturated solution of thiourea is added. After 1-2 minutes gold thiooxinate dissolves completely and liberates the coprecipitated rhenium thiooxinate which is then extracted with chloroform.

Copper is permissible in amounts of 4-5 mg. When large amounts of Cu are present low results are obtained for rhenium because of complexing of the thiooxine.

Tin (II) in large amounts reduced perrhenate to the lower valence states and interferes with Re determination. An amount equaling 5 mg of Sn (II) is permissible. Tin (IV) is permissible in amounts of 50 mg.

Large amounts of Ni, Co, Zn, Cd, In, Sb, Bi, Mn, U, Pb, Tl^1, Ge, Nb, Ta, Ga, Al, Zr, Th, Cr^{III}, and the rare earths do not enterfere with the determination of rhenium. Large amounts of the salts of the alkali and alkaline earth elements do not affect the accuracy of the rhenium determination.

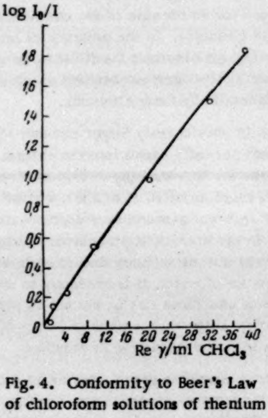

Fig. 4. Conformity to Beer's Law of chloroform solutions of rhenium thiooxinate (measurements made on a SF-4 spectrophotometer at 438 mμ).

Results for the determination of rhenium in the presence of foreign elements are given in Table 2.

The Effect of Anions on the Accuracy of Rhenium Determination. As is evident from the results given in Table 3, the anions which one normally meets in analytical practice (bromides, iodides, fluorides, sulfates, phosphates, perchlorates, etc.), even when present in significant amounts, do not interfere with the determination of rhenium, with the exception of large amounts of arsenates and hypophosphites. Arsenites should be absent. Nitrates and other oxidizing agents should also be absent.

Determination of Rhenium in Synthetic Mixtures. During determination of rhenium in complex mixtures, the limiting permissible amounts of foreign elements (results given in Table 2) decrease. Nevertheless, determination of rhenium is possible in the presence of mixtures of considerably larger amounts of a number of elements as is evident from the examples given in Table 4.

Analytical Procedure. To 8 ml of the test solution contained in a 100 ml Erlenmeyer flask 37 ml of concentrated HCl is added, and after mixing, 5 ml of a 6% solution of thiooxine hydrochloride in concentrated hydrochloric acid (6 g of thiooxine hydrochloride is dissolved in 100 ml concentrated HCl). The flask is placed in a boiling water bath for 3 minutes (no more). It is then immediately well cooled under the tap, and the solution is poured into a 100 ml separating funnel. Rhenium thiooxinate is extracted by intensive shaking with 5 ml (or 10 ml depending on the Re content) of chloroform. After the layers have separated out, the chloroform is removed as completely as possible and transferred into another separating funnel containing 22 ml of 9 N HCl (4 ml H_2O + 18 ml concentrated HCl sp. gr., 1.193). The mixture is thoroughly shaken for 2 minutes and then 2.5 ml of the thiooxine solution mentioned above added and the whole shaken for another 2-3 minutes. After the chloroform layer has separated out it is transferred into a test tube and dried for 1-2 minutes, with one or two granules of anhydrous calcium chloride (the $CaCl_2$ should not have an alkaline reaction). It is finally measured photometrically in a 1 cm cuvette at 438 mμ. The amount of Re present is determined by means of a calibration curve constructed under similar conditions. It is best to construct the calibration curve when 50-100 mg of noninterfering elements (Ni, Co, Zn, etc.) are present in solution, since under these conditions, it is probable that as a result of changes in the solubility of the chloroform in the mixture, the extinction of the extracts changes slightly.

When iron is absent or when it is present in small amounts in the test solution, washing of the extract with 9 N HCl can be omitted. When this technique is adopted, in order to free the extract from aqueous turbidity, it is best to filter it through well-dried glass wool, since some types of anhydrous $CaCl_2$ (becasue of their alkaline reaction) destroy the color of the rhenium complex.

SUMMARY

Under different conditions, thiooxine forms inner complex salts of different colors with rhenium. The very stable rhenium thiooxinate which is formed in 5-11.75 N HCl permits determination of very small amounts of rhenium by a photometric method.

A very selective photometric method has been developed for the determination of Re at concentrations of 5-200 γ and more in the presence of 5000 times its amount of Mo, in the presence of 500 times its amount of W, and in the presence of considerably larger amounts of other elements.

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CHROMATOGRAPHIC ANALYSIS OF MIXTURES OF C_5 HYDROCARBONS

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During the catalytic dehydrogenation of isopentane to isoamylenes and isoprene there is formed a mixture consisting of liquid C_5 hydrocarbons, both saturated and unsaturated, in which gaseous hydrocarbons are usually dissolved. Analysis of such multicomponent mixtures with composition C_1-C_5 has hitherto been realized by various methods. The concentration of the gaseous C_1-C_4 hydrocarbons can be determined by different methods including gas chromatography [1]. The bromometric methods of Rosenmund [2], and Gal'pern [2, 3] are used for the determination of the total content of unsaturated hydrocarbons in mixtures of C_5 hydrocarbons. The piperylene and isoprene content can be found by means of the reaction with maleic anhydride [4]. In addition, isoprene can be determined separately from piperylene by the method of Robey and Wiese [2, 5]. During a study of the catalytic dehydrogenation of the isopentane fraction of a light benzine, Mamedaliev et al. [6] established the composition of the unsaturated part of the catalyzate by means of a bromination reaction. Shuikin et al. [7] carried out accurate fractionation of the isopentane catalyzates, and identified individual hydrocarbons in the fractions by means of a combination of light scattering spectra and infrared spectra. Kazanskii et al. [8] during a study of the composition of the catalyzates, isolated on a fractionating column a fraction with a boiling range of 20--38°, which, after treatment with maleic anhydride, was examined by means of their combination light scattering spectra. Gorin et al. [9] during a study of isopentane catalyzates also used accurate fractionation and infrared spectra, while the fraction of catalyzate additionally treated with maleic anhydride was studied by its oxidation with permanganate solution. Thus, analysis of mixtures of C_5 hydrocarbons is a complex and difficult problem. The aim of the work described here was to develop a rapid and fairly simple method for the quantitative analysis of isopentane-isoprene-isoamylene mixtures. For this purpose we used gas-liquid partition chromatography [10] and chromathermography [11]. By combining these methods we succeeded in developing a method for the quantitative analysis of C_5 hydrocarbons in the presence of lighter hydrocarbons.

EXPERIMENTAL

Hydrocarbons. Isopentane, 2-methylbutene-2, 2-methyl-and 3-methylbutene-1, and isoprene prepared in a pure state previously [2] were used for the work. Normal pentane was isolated from a petroleum pentane fraction by fractionation on a column with an efficiency of 30 theoretical plates; it had a boiling point of 36.1° (760 mm), n_D^{20} 1.3574, d_4^{20} 0.6256. Pentene-1 was synthesized from ethyl magnesium bromide and allyl chloride [12]. Pentene-2 was obtained by pyrolysis of pentanol-3 acetate. The normal pentenes after fractionation on a column with an efficiency of 40 theoretical plates had the following constants: pentene-1, bp 29.0° (760 mm), n_D^{20} 1.3717; d_4^{20} 0.6403; pentane-2, bp 36.2 (760 mm), n_D^{20} 1. 3800; d_4^{20} 0 6498 (mixture of the cis- and trans- forms). The preparations of the piperylenes used had the following constants: cis-piperylene- bp 44.2° (760 mm); n_D^{20} 1.4356; d_4^{20} 0.6927; trans-piperylene- bp 42.2° (760 mm), n_D^{20} 1.4295, d_4^{20} 0.6767.

Analytical Procedure. Development of a chromatographic technique for analyzing the hydrocarbons was carried out using individual hydrocarbons and synthetic mixtures of these hydrocarbons which had been evaporated beforehand in air.

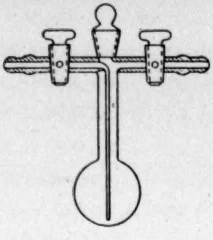

Fig. 1. Microevaporator.

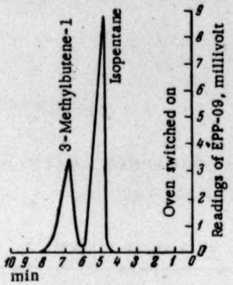

Fig. 2. Chromatogram of mixture No. 12 (chromathermograph on alumina).

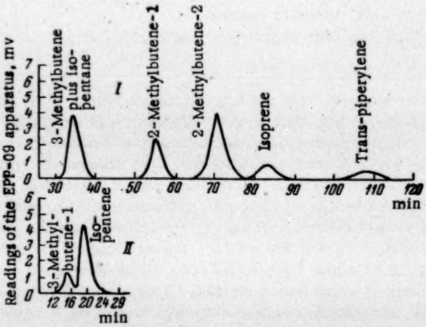

Fig. 3. Chromatogram of Mixture No. 25: 1) Main experiment (chromathermography on alumina coupled with gas liquid partition chromatography on diatomaceous earth impregnated with dibutyl phthalate); 2) supplementary experiment for separating 3-methylbutene-1 and isopentane by gas-liquid chromatography on diatomaceous earth impregnated with vaseline oil.

We chose two methods for preparing air-hydrocarbon mixtures. The first method was evaporation of the hydrocarbons in air by means of a microevaporator (Fig. 1). The test mixture of the hydrocarbons was placed in the evaporator and air (2-3 liters) passed through it while the flask of the apparatus was heated over an alcohol burner. The mixture of air plus vapors of hydrocarbons was collected in a gas holder over brine, from which samples were then taken for analysis on the chromatograph.

In the other method the hydrocarbon test mixture was introduced into a small, thin-walled spherical ampoule, which, after it had been sealed, was broken in an evacuated vessel provided with a two-way tap. In this method mixtures of hydrocarbon vapors with a small amount of air were obtained. In this way samples of air-hydrocarbon mixtures from the catalyzates obtained by the the dehydrogentation of isopentane and light benzine fractions were prepared.

Both methods of preparing samples are of equal value, since the greatest deviation of the experimental results obtained by the two methods amounted to 5% relative.

A universal chromathermograph [13] was used for analyzing the hydrocarbon mixtures. In this apparatus simultaneous chromathermographic separation on aluminum oxide, and gas liquid partition chromatographic separation on diatomaceous earth impregnated with dibutyl phthalate (25% by weight of the supporting phase) was effected. The particle size of the support was 0.5-1 mm. A 70-80-cm column of alumina was used and a 10 meter column of the diatomaceous earth. The cross section of the sorption columns was 0.125 cm^2.

For the chromathermographic separation the moving temperature gradient was established by means of an electric oven with a temperature drop of 2° per cm length of the oven. The distribution of the temperature along the oven was 20 to 120°. The temperature of the oven with the column of diatomaceous earth was kept constant with an accuracy of 1°. Air purified from water vapor and from acid and combustible vapors was used as the mobile phase. Its linear velocity was measured with a rheometer and was constant in individual experiments within the limits 120-200 cm/min. All the experiments were carried out under reduced pressure.

TABLE 1

Analysis of Hydrocarbon Mixtures

Composition of the mixture	Taken, weight, %	Found							
		area measured by planimeter	absolute error, %	$\theta = 0,5$; $K_\theta = 1,065$, wt., %	$\theta = 0,75$; $K_\theta = 1,66$; weight %	$\theta = 0,75$; $K_\theta = 1,66$, weight, %	absolute error, %	$\theta = 0,9$; $K_\theta = 2,73$, weight, %	absolute error, %
Ten-component synthetic mixture No. 18									
Isopentane + 3-methylbutene-1	30,6	30,3	−0,3	29,1	−1,5	28,4	−2,2	27,7	−2,9
n-Pentane	5,8	5,2	−0,6	5,4	−0,4	5,6	−0,2	5,6	−0,2
Pentene-1	6,2	6,4	+0,2	7,1	+0,9	7,1	+0,9	7,0	+0,8
2-Methylbutene-1	15,4	13,8	−1,6	13,7	−1,7	13,6	−1,8	13,3	−2,1
Pentene-2	6,1	6,1	0,0	6,6	+0,5	6,3	+0,2	6,1	0,0
2-Methylbutene-2	16,3	18,9	+2,6	18,7	+2,4	19,0	+2,7	18,7	+2,4
Isoprene	6,4	6,3	−0,1	6,1	−0,3	6,3	−0,1	6,8	+0,4
trans-Pilerylene	6,5	6,5	0,0	6,5	0,0	6,8	+0,3	7,4	+0,9
cis-Piperylene	6,7	6,5	−0,2	6,8	+0,1	6,9	+0,2	7,4	+0,7
Catalyzate No. 17									
Propane		8,0		7,3	−0,7	7,3	−0,7	8,5	+0,5
Propylene		2,9		3,4	+0,5	3,5	+0,6	3,9	+1,0
Isobutane		2,5		2,8	+0,3	2,7	+0,2	3,3	+0,8
n-Butane		2,1		2,5	+0,4	2,7	+0,6	2,6	+0,5
Isobutylene-butene-1		6,0		5,8	−0,2	6,1	+0,1	6,1	+0,1
trans-Butene-2		1,4		1,2	−0,2	1,3	−0,1	1,5	+0,1
cis-Butene-2		1,0		1,1	+0,1	1,3	+0,3	1,4	+0,4
Isopentane		33,5		34,6	+1,1	34,2	+0,7	31,8	−1,7
3-Methylbutene-1		2,9		2,6	−0,3	2,6	−0,3	2,8	−0,1
n-Pentane		2,0		2,2	+0,2	2,2	+0,2	2,0	0,0
Pentene-1		0,9		0,9	0,0	0,9	0,0	0,8	−0,1
2-Methylbutene-1		10,0		10,0	0,0	9,7	−0,3	9,5	−0,5
Pentene-2		2,7		2,7	0,0	2,6	−0,1	3,7	+1,0
2-Methylbutene-2		21,0		21,5	−0,5	21,2	−0,8	20,0	−2,0
Isoprene		2,1		1,4	−0,7	1,7	−0,4	2,1	0,0
Pentane-amylene fraction									
Isopentane		54,1		52,7	−1,4	52,8	−1,3	53,0	−1,1
n-Pentane		13,7		13,5	−0,2	14,0	+0,3	13,7	0,0
Pentene-1		0,5		0,5	0,0	0,5	0,0	0,5	0,0
2-Methylbutene-1		2,5		3,7	+1,2	3,5	+1,0	3,5	+1,0
Pentene-2		10,6		11,1	+0,5	10,5	−0,1	10,0	−0,6
2-Methylbutene-2		17,7		17,6	−0,1	17,8	+0,1	18,3	+0,6
trans-Piperylene		0,9		0,9	0,0	0,9	0,0	1,0	+0,1

TABLE 2

Analysis of Synthetic Mixtures of Hydrocarbons

	Components	Taken, wt, %	Found weight,%	Absolute error, %	Mixt. no.	Components	Taken, wt, %	Found, weight,%	Absolute error,%
4	Isopentane	54,4	53,7	−0,7	14	Isopentane	81,2	80,5	−0,7
	2-Methylbutene-2	45,6	46,3	+0,7		Pentene-2	18,8	19,5	+0,7
7	Isopentane	83,7	83,6	−0,1	16	Isoprene	50,1	48,9	−1,2
	n-Pentane	16,3	16,4	+0,1		trans-Piperylene	49,9	51,1	+1,2
8	Isopentane	35,0	36,8	+1,8	25	Isopentane	34,7	34,3	−0,4
	n-Pentane	11,5	11,8	+0,3		3-Methylbutene-1	11,4	11,4	0,0
	2-Methylbutene-2	35,0	32,7	−2,3		2-Methylbutene-1	13,4	13,5	+0,1
	2-Methylbutene-1	18,5	18,7	+0,2		2-Methylbutene-2	25,5	28,1	+2,6
10	Isopentane	79,1	80,5	+1,4		Isoprene	7,2	5,6	−1,6
	2-Methylbutene-1	20,9	19,5	−1,4		trans-Piperylene	7,8	7,1	−0,7
12	Isopentane	83,9	85,8	+1,9					
	3-Methylbutene-1	16,1	14,2	−1,9					

•Note: The area of the elution curves was measured by means of a PP-2K planimeter.

TABLE 3

Composition	Taken, wt, %	Found, weight, %							Mean wt., %	Max. deviation results from mean, rel., %	Deviation from taken, abs, %
		126	128	129	130	131	132	133			
Isopentane + 3-methylbutene-1	30,6	30,4	30,2	31,1	31,3	28,7	30,3	30,3	30,3	5	−0,3
n-Pentane	5,8	5,1	5,3	5,2	5,1	5,2	5,2	5,6	5,2	8	−0,6
Pentene-1	6,2	6,4	6,5	6,8	5,8	6,4	6,2	6,6	6,4	9	+0,2
2-Methylbutene-1	15,4	13,8	13,5	13,5	13,1	13,8	14,9	14,0	13,8	5	−1,6
Pentene-2	6,1	5,8	6,3	5,9	6,2	6,2	6,2	6,3	6,1	5	0,0
2-Methylbutene-2	16,3	19,8	19,6	18,1	19,3	19,8	17,6	18,4	18,9	7	+2,6
Isoprene	6,4	6,1	5,9	6,3	6,4	6,4	6,8	6,0	6,3	8	−0,1
trans-Piperylene	6,5	6,6	6,3	6,2	6,6	7,0	6,8	6,1	6,5	8	0,0
cis-Piperylene	6,7	6,0	6,4	6,9	6,2	6,5	7,0	6,7	6,5	8	−0,2

TABLE 4

Determination of Impurities

Composition of sample analyzed	Gas benzine I, weight %	Gas benzine II, weight %	Isopentane from a natural gas condensate, weight %
Propane	0.1	0.3	–
Isobutane	0.5	0.4	–
n-Butane	2.4	2.7	1.0
trans-Butene-2	1.0	1.0	–
cis-Butene-2	1.9	1.5	–
Isopentane	88.6	93.1	98.6
3-Methylbutene-1	0.4	0.8	–
n-Pentane	1.0	–	0.4
Pentene-1	0.5	–	–
2-Methylbutene-1	1.1	0.1	–
Pentene-2	1.1	–	–
2-Methylbutene-2	1.4	0.1	–

Determination of the concentration of the components of the mixture after passing through the column was based on measurement of the thermal conductivity of the gases, and the presence of very small amounts of impurities was established on the basis of the thermal effect obtained on burning the components of the mixture. The readings of the apparatus were automatically recorded by means of an ÉPP-09 potentiometer with a 10 millivolt scale. An analysis took about 2 hours. From 5 to 15 ml of the air-hydrocarbon mixture prepared beforehand from the test samples was taken for an analysis. The order and elution time of the hydrocarbons were established by means of individual components, and from the analysis of synthetic mixtures. The calibration curves for the apparatus were used for calculating the composition of the mixtures. The content of each component in a mixture was calculated on the basis of the ratio of the area under the peak of a particular component to the total area under all the peaks on the chromatogram.

Treatment of the Elution Curves. For characterizing the degree of chromatographic separation, the adsorption coefficient G, the width of the band of the adsorbate μ, the distance between the maxima on the elution curve Δx, and the partition factor K_1 [14] are of essential importance.

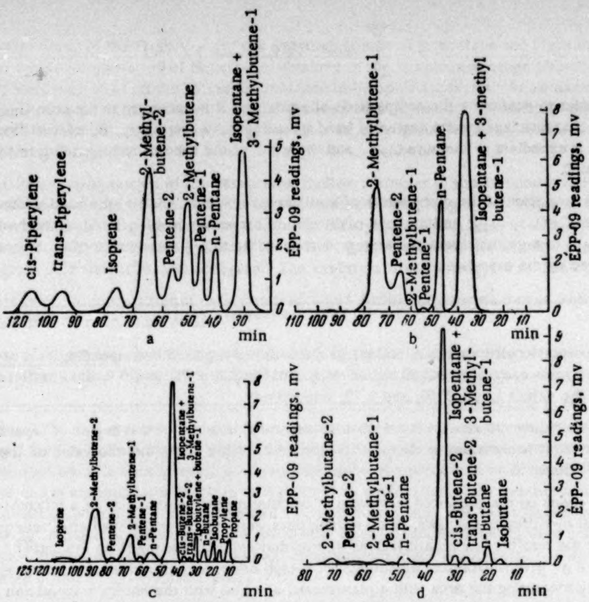

Fig. 4. Chromatograms for complex hydrocarbon mixtures: a) Synthetic mixture No. 18; b) catalyzate from isopentane dehydrogenation; c) pentane-amylene fraction from catalytic cracking benzine; d) gas benzine I bp. 20-39°.

An important element in chromatographic analysis is the deciphering of the elution curve, which depends on the physicochemical magnitudes indicated. The best assessment of the content of the components in a mixture can be obtained by measuring the area under the elution curve. Direct measurement of the area is simple in the case where complete separation of a mixture has been effected. The errors increase, however, when it is necessary to determine low concentrations and where the peaks on the curve overlap each other. Various techniques are used for measuring the areas. For example [15] the measurement of the area of the curve is replaced by determining the concentration at the maximum of the elution curve. In this case it becomes necessary to ensure strict observation of the experimental parameters and of the calibration for all the individual components of a mixture. In some papers [16] the area of a bell-shaped peak is calculated by measuring the area of a triangle, approximating in area to that of the peak, the area being taken as the products of the peak height and the width of the peak at the point where the concentration $C = 0.5\ C_{\max}$. Such an approximation is quite sufficient when the components of the mixture are completely separated. However, it is not applicable in practice when the partition factor $K_1 < 1/2$ [14].

In the present article a method for decipering the elution curve is suggested which is based on the assumption that the Gaussian distribution is applicable to the linear adsorption [17].

$$C = C_{\max} e^{-\rho x^2}. \qquad (1)$$

The value of ρ determines the degree of band spreading and depends on the experimental parameters, while $x = V - V_m$; here V and V_m are the volumes of the carrier gas corresponding to a given concentration C of a material and the concentration of the material at the maximum of the curve $C_{\max}$. It is obvious that the amount of the components of a mixture q can be calculated by means of the following equation:

$$q = \int_{-\infty}^{+\infty} C_{\max} e^{-\rho x^2} dx = C_{\max} \sqrt{\frac{\pi}{\rho}}. \qquad (2)$$

Thus, in order to determine the composition of a mixture, it is necessary to measure C_{max} and ρ. The width of the band μ is characterized by the degree of band spreading ρ. Accordingly, in order to find the area of the elution curves it is expedient to measure C_{max} and the width of the band μ corresponding to the various values of the concentration C.

When good resolution of the components of a mixture is achieved ($K_1 > 1$) the band width should be determined at the point where $C = 0.5\ C_{max}$, and the area of the elution curve can be calculated on the basis of measurements of C_{max} and $\mu_{0.5}$. In a general form, the area q, corresponding to a given amount of a component in a mixture, will be determined by the expression:

$$q = K_\theta C_{\max} \mu_\theta, \qquad (3)$$

where K_θ is the proportionality constant, and μ_θ is the width of the band corresponding to a given point of the curve at which the ratio $c/c_{max} = \theta$. At values of θ equal to 0.5, 0.75, and 0.9, the coefficient K_θ, as calculations show, has the values 1.065, 1.66, and 2.73, respectively.

In order to calculate the area of the elution curve, which depends on the degree of separation of the components of a mixture, it is necessary to choose the appropriate value of K_θ and the value of μ_θ corresponding to it from the three values.

In order to check on the suggested technique of calculating the composition of a mixture the area was calculated in parallel by different methods. Such calculations were made for the synthetic, ten-component mixture No. 18 (Table 1); the results of such calculations showed that calculations made on the basis of equation (3), using various values of K_θ, give satisfactory agreement with each other, and also give satisfactory agreement with the results obtained by measuring the area with a planimeter, and also with the known composition of the synthetic mixture. The same result was obtained on treating about 30 elution curves for catalyzates obtained by the dehydrogenation of isopentane and light benzine fractions. Examples of these calculations are shown in Table 1.

Investigation of Synthetic Mixtures. The experimental data obtained during analysis of synthetic mixtures are given in Table 2. The results given indicate satisfactory analytical results for binary and more complex hydrocarbon mixtures, consisting of C_5 paraffins, olefins, and both normal and iso-dienes. Of all the combinations of hydrocarbons (Table 2) only two of them, namely: 3-methylbutene-1 and isopentane could not be separated under the conditions employed. However, this pair of hydrocarbons can be clearly separated by chromathermography on alumina (linear velocity of air current 120 cm/min when the heat field is moved at a rate of 7.1 cm/min) or on a gas-liquid chromatographic column filled with diatomaceous earth carrying petroleum jelly oil as the stationary phase.

In Fig. 2 is shown the separation of mixture No. 12 under chromathermographic conditions. The use of the second technique for determining 3-methylbutene-1 and isopentane when they are present together in a mixture is illustrated on the chromatograms for the complex mixture of C_5 hydrocarbons (mixture No. 25, Fig. 3). In the upper part of this diagram separation of the mixture on two sorbents is shown. Here 3-methylbutene-1 and isopentane are not separated but form a common peak. In the lower part of the diagram the separation of the mixture on a 3.5 meter column of diatomaceous earth impregnated with petroleum jelly oil is shown. In this part of the diagram there are two peaks corresponding to isopentane and 3-methylbutene-1.

The analysis of an even more complicated mixture, namely No. 18, and also the reproducibility of the results are shown in Table 3. The results given indicate the satisfactory reproducibility of a determination within the limits of 5-9% relative. The chromatogram of this mixture is given in Fig. 4a, in which is clearly seen the separation of the components of the mixture, and the order in which they emerge.

From the analytical results adduced for the synthetic mixtures it follows that the mean maximum deviation amounts to about 10% relative, whereas the deviation from the concentrations of the components taken varies from 0 to 2.6% absolute, depending on the value of the concentrations of the hydrocarbons.

Chromatographic Study of the Products from the Dehydrogenation of Isopentane and Light Benzine Fractions. 35 catalyzates from the dehydrogenation of isopentane, obtained in the temperature range 500-550° and at volume rates of 0.5-2 hr $^{-1}$, were examined on the universal chromathermographic apparatus. As an example there is shown in Fig. 4b the elution curve for catalyzate No. 17 obtained on an alumochrompotassium catalyst at 550°, and a volume rate of 1 hr $^{-1}$. Under the analytical conditons used, only isobutylene and butene-1 were not separated. The detailed quantitative composition of the catalyzate is given in Table 1.

Since the qualitative composition of the catalyzates studied is similar to the composition of light-cracking benzines, a study was made of a number of benzine fractions whose boiling ranges are similar to those of the test hydrocarbons. For example, the pentane-amylene fraction of catalytic cracking benzine with a boiling range of 26-39° (d_4^{20} 0.6335, n_D^{20} 1.3651; unsaturated hydrocarbons content calculated from the bromine number 33.8, and from the chromatogram 32.2 weight%), was analyzed. The analytical results are given in Table 1 and in Fig. 4c.

Results of a study of the composition of catalyzates obtained during dehydrogenation of isopentane and benzine fractions will be published later in more detail.

Determination of Impurities. A very important problem in the study of the catalytic processes of treating hydrocarbons is the determination of small amounts of impurities in the basic products.

The universal apparatus permits detection of very small amounts of materials, thanks to the application of chromathermography [17]. The concentration of materials occurs during chromathermographic separation because of the compression of the band of adsorbate. When only 10-15 ml of gas is introduced onto the adsorbent, as the present investigation showed, it is even possible to determine tenths of a percent of an impurity in the basic product. When large volumes of gas are used (100-200 ml), it is possible to detect hundredths and thousandths of a percent of an impurity. For this purpose light benzine obtained by catalytic cracking was fractionated on a laboratory column, and the 20-39° fraction (gas benzine I) and the 20-27° fraction (gas benzine II) were collected. These benzine fractions were studied by means of the universal chromathermographic apparatus. At the same time, isopentane obtained from a natural gas condensate was analyzed.

Results of the study of the impurities are given in Table 4. They indicate that even on analyzing only 10 ml of an air-hydrocarbon mixture, it is possible to detect tenths of a percent of an impurity. The general appearance of the chromatogram for the hydrocarbon mixture containing impurities is shown in Fig. 4b, d.

SUMMARY

A technique has been developed for analyzing C_5 hydrocarbon on a universal apparatus, in which chromathermography is combined with gas liquid chromatography.

A simple method is suggested for calculating the composition of hydrocarbon mixtures from the chromatograms corresponding to complete as well as to incomplete resolution of the components.

It has been shown that by the combined use of chromathermography and gas liquid chromatography it is possible to establish accurately the composition of catalyzates obtained by dehydrogenation of isopentane, and the composition of light benzine fractions, and to determine small amounts of impurities in them.

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THE EFFECT OF THE RATIO OF THE ORIGINAL CONCENTRATIONS OF THE IONS BEING SEPARATED CHROMATOGRAPHICALLY ON THE NATURE OF PRECIPITATION CHROMATOGRAMS

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E. N. Gapon and I. M. Belen'kaya [1] while considering the basic laws of precipitation chromatography of ions emphasize that the sequence of the distribution of precipitates in chromatograms depends primarily on whether the mixture to be chromatographed is poured into the column containing the precipitant, or, on the other hand, whether the precipitant is poured into the column containing the mixture. On the basis of experimental results obtained during the separation of certain cations in the form of their iodides (equimolar solutions of the cations, in which their ratio of concentration ranges from 1: 9) the authors established that in the first case the order of the distribution of the zones in the chromatograms is determined by the solubility product. It is considered thereby [1] that the order of the zones does not only depend on the concentration of the precipitant in the column, but also on the concentrations and ratios of the concentrations of the ions to be chromatographed in the mixture. On the other hand, it is known [2] that during the precipitation of mixtures of ions from solution by some precipitant, the order in which precipitates is formed depends not only on the amount present but also on the ratio of the concentrations of the materials in solution. This conclusion is also applicable to precipitation chromatography.

In order to clarify the effect of the ratio of the original concentrations of the ions to be chromatographed on the chromatographic process, let us consider the following example. If we have a mixture of salts M_1X and M_2X and we precipitate them by means of a common precipitant RZ, then the following reactions will occur:

$$M_1X + RZ = M_1Z + RX$$
$$M_2X + RZ = M_2Z + RX.$$

In a saturated solution of these salts the following equilibriums are established:

$$[M_1]\,[Z] = L_{sM_1Z}$$
$$[M_2]\,[Z] = L_{sM_2Z}$$

Since both precipitates are in contact with the same solution, the equilibrium concentration of the precipitating ion should simultaneously satisfy both equations. Dividing one equation by the other, we get:

$$[M_1]^\circ/[M_2]^\circ = L_{s\,M_1Z}/L_{s\,M_2Z} = k \qquad (1)$$

In a saturated solution the ratio of the concentrations of the substances M_1X and M_2X is a constant, and any breakdown in this ratio leads to a process which will restore it. Under such conditions, if the ratio of the concentrations of the substances is 1: 1, then, depending on the amount of the precipitates obtained, we will have the following three cases:

a) L_{sM_1Z}, $< L_{sM_2}Z$. In this case, according to Equation (1), M_1Z is first formed, and then M_2Z.

b) $L_{sM_1Z} > L_{sM_2Z}$. This is the reverse of the first case.

c) $L_{sM_1Z} \approx L_{sM_2Z}$. In this case the precipitates of the materials will be obtained simultaneously.

When the materials are precipitated in a chromatographic column previously soaked with precipitant, the order of formation of the zones will depend, in all cases, on the value of the solubility product.*

When, however, the ratio of the original concentrations is not equal to 1 : 1, but changes within wide limits, then, depending on the values of the solubility product, we will have the following cases:

1. For $L_{sM_1Z} < L_{sM_2Z}$

a) $[M_1] > [M_2]$, accordingly $[M_1]/[M_2] > K = \lambda$.

It follows from Equation (1) that during chromatographic separation of such a mixture, M_1X will be precipitated first, as a result of which the concentration $[M_1]$ will decrease. At the point where the Relation (1) is obtained, simultaneous precipitation of M_1X and M_2X will start. Precipitation of the two ions will finish simultaneously. During chromatographic separation two zones will be obtained, the first consisting of a precipitate of M_1Z, and a second zone consisting of a mixture of the two precipitates M_1Z and M_2Z.**

b) $[M_1] = [M_2]$, accordingly $[M_1]/[M_2] > K = \lambda_1$.

This case can be related to the first.

c) $[M_1] < [M_2]$, accordingly $[M_1]/[M_2] = K$.

It follows from Equation (1) that precipitation of materials M_1X and M_2X starts and finishes simultaneously. During chromatographic separation, only one, a mixed zone of the precipitates M_1Z and M_2Z, is obtained, i. e., separation of these materials is impossible.

d) $[M_1] \ll [M_2]$, accordingly, $[M_1]/[M_2] < K = \lambda_2$.

In this case material M_2Z is first precipitated until Equation (1) is satisfied, after which simultaneous precipitation of both M_1X and M_2X starts. As a result of a chromatographic separation a pure zone consisting of a precipitate of M_2Z is obtained, together with a mixed zone consisting of precipitates M_1Z and M_2Z.

2. For $L_{sM_1Z} > L_{sM_2Z}$ the same phenomena are observed in the reverse order.

3. For $L_{sM_1Z} = L_{sM_2Z}$ the following three cases are possible.

a) $[M_1] > [M_2]$, accordingly $[M_1]/[M_2] > K = \lambda'$.

According to Equation (1), during chromatographic separation, a pure zone consisting of M_1Z is formed, followed by a mixed (1:1) zone consisting of M_1Z and M_2Z.

b) $[M_1] = M_2]$, accordingly $[M_1]/[M_2] = K$.

In this case, during chromatographic separation, there is formed a mixed zone (1:1) consisting of precipitates M_1Z and M_2Z.

c) $[M_1] < [M_2]$, accordingly $[M_1]/[M_2] < K = \lambda_1'$.

This case is the reverse of the first.

We have been able to establish these conclusions experimentally during the separation of components.

In the first series of experiments we used 40% solutions of KI and KBr and a 0.5 N solution of $AgNO_3$. In the second series 20% solutions of KBr and KCl and a 0.1 N $AgNO_3$ solution were used. Precipitation was carried out on Schleicher-Schull paper 2043-b impregnated beforehand with the precipitant. At ratios of the concentrations of the ions I^-: Br^- up to $1:2.06 \times 10^3$* the order in which the zones were formed depended on L_s (the yellow zone of AgI was formed first, this being followed by the grayish-blue zone of AgBr.** When the ratio of the concentrations was $1:2.06 \times 10^3$ a mixed zone of the two precipitates was obtained, while above this ratio, the order of the zones changed. The same phenomena were observed during separation of Br^- and Cl^- ions, the only difference being that the shift in the position of the zones occured at a ratio of the concentrations of the ions $Br^-:Cl^-$ greater than $1:0.34 \times 10^3$.*** Similar experiments with precipitates having the same values for their solubility product were not carried out because we could not choose ions which would give differently colored precipitates.

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* It is assumed here that no other factors such as adsorption, coprecipitation, hydrolysis, complex formation, etc., are operative.

** The amount of M_1Z in the second zone will depend on the difference in the solubility products L_s of the precipitates. For large differences in the solubility products the second zone can be considered in practice as consisting only of substance M_2Z.

The fundamental law of precipitation chromatography [3] should be formulated as follows: any material (precipitant) capable of interacting with a solution of a series of other materials (the materials being chromatographed) placed on any highly dispersed material (carrier), will form a precipitation chromatogram, as long as the solubility products of the precipitates differ from each other, and the ratio of the original concentrations of the materials in the mixture being chromatographed satisfies certain definite values.

SUMMARY

A necessary condition for the almost complete separation of two materials by means of precipitation chromatography is that there should be a difference between the solubility products of the precipitates formed; the order in which the zones on the chromatogram are formed depends on the solubility product.

A difference in the solubility products of the precipitates formed is a necessary, but not a sufficient condition for their separation. The ratio of the original concentrations of the materials to be separated chromatographically also affects the separation of the materials and the order in which the zones are formed.

During the separation of a mixture of materials by means of precipitation chromatography, a pure zone will only be obtained for that material which has the lowest solubility product.

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* The difference between the solubility product L_s of AgI and AgBr is 2.1×10^{-3}

** Observations of the chromatograms should be made immediately after development, since secondary phenomena appear as time elapses.

*** The difference between the solubility product L_s of AgBr and AgCl is 0.34×10^{-3}.

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BRIEF COMMUNICATIONS

PHOTOMETRIC DETERMINATION OF NAPHTHIONIC ACID IN TECHNICAL 1,4-NAPHTHOLSULFONIC ACID

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1, 4-Naphtholsulfonic acid which is used in dye production is obtained by Bucherer's method [1] from naphthionic acid; the product obtained invariably contains a few percent of the original naphthionic acid. Two methods have been suggested for determining the latter [2, 3]. These methods are, however, not sufficiently accurate and sensitive. The photometric method we would like to put forward differs from that of A. I. Nelyubina [3] in the following respects: the amount of nitrite taken is sufficient for complete diazotization of the aminosulfonic acid and for the nitrosation of the hydroxysulfonic acid; the azo component chosen is 1, 8-aminonaphthol-2,4-disulfonic acid (acid CC) with which is obtained a purple dye differing strongly in shade from the orange-yellow of the C-nitroso compound; the concentration of the dye is measured photometrically, a yellow filter being introduced for excluding absorption of the nitroso compound. In this form the method also proved to be suitable for studying the kinetics of the Bucherer reaction. The method can also be used in other cases where it is necessary to determine primary aromatic amines in mixtures with hydroxy derivatives.

The absorption maximum of solutions of the dye is located at 540 mμ; however, the nitroso compound also absorbs strongly in this region; accordingly, during measurement of the optical density, a yellow filter with maximum transmission at about 580 mμ was used.

The optimum medium for carrying out azo coupling proved to be a bicarbonate buffer solution with a pH of 7.5. The coupling itself finishes rapidly, but on allowing the dye solution to stand for several hours irreversible changes occur which become manifest in an increase in the optical density.

Determination of Naphthionic Acid in the Finished Product

The nitroso compound from 1, 4-naphtholsulfonic acid absorbs light passed by the yellow filter ($\lambda_m = 579$ mμ) to a measurable extent. Accordingly, during construction of the calibration curve and when carrying out determinations, the naphtholsulfonic acid concentration of the solutions should be constant. During the analysis of technical samples this requirement can only be fulfilled approximately, since normally only the nitrite number is known and this only characterizes the total content of both sulfonic acids; the error arising from this circumstance, however, can be ignored.

The following original solutions are prepared in order to construct a calibration curve: I) 0.2 N $NaNO_2$ solution; II) 0.02 M sulfonic acid CC (the azo component); III) 0.002 M sodium naphthionate; IV) a solution of zinc salt of 1,4-naphtholsulfonic acid (0.01 equivalents/liter). 50 ml lots of solution IV are taken and the following amounts of solutions III:

Volume of solution III, ml	0	2	5	10	15	20
Ratio of naphthionic acid to naphtholsulfonic acid, %	0	0,8	2	4	6	8

To the mixture obtained is added 50 ml of water and the solution heated to 40-50°. Almost all the requisite amount of nitrite (2.3 ml) is then added; this is followed, with stirring, with 2 ml of concentrated hydrochloric

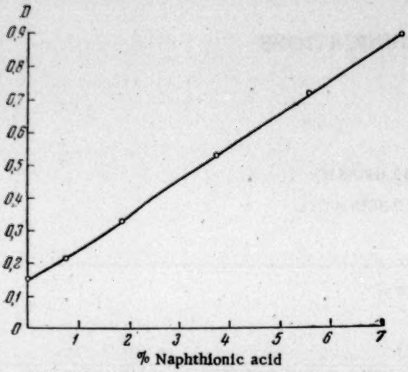

Fig. 1. Calibration curve for determination of naphthionic acid in 1, 4-naphtholsulfinic acid.

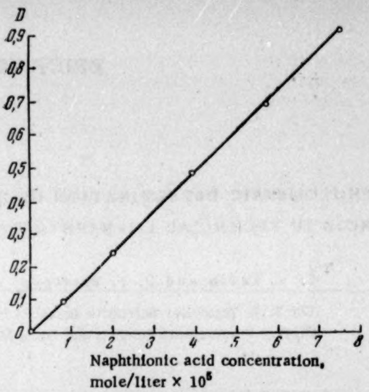

Fig. 2. Calibration curve for determination of the content of naphthionic acid in a reaction mass during the Bucherer reaction.

acid; the solution is finally titrated with nitrite until there is a distinct reaction to iodide-starch paper after 10 minutes. A quantity equaling (m + 1) 500-ml standard flasks are taken for m synthetic mixtures. Into each of them is introduced 5 ml of solution II, 100 ml of water, and 3 g of $NaHCO_3$ and the whole shaken up until the latter has dissolved; m flasks are used for coupling, for this purpose into each flask is poured slowly, with stirring, one of the prepared portions of diazo compound. After 20 minutes the volume is made up to the mark with water. The solutions obtained, containing the dye and the nitroso compound, have colors ranging from brownish-yellow to intense red.

The remaining flask is used for comparison; water is added to it to bring the volume to the mark.

In order to measure the optical density on the TsZ-A apparatus all the solutions (including the reference solution) must be diluted five times.*

The optical density of the solutions is measured and a calibration curve constructed (Fig. 1).

During the analysis of an unknown sample the total content of both sulfonic acids is determined by the nitrite method (q%). An aliquot of 246.2 x 0.005 x 100 /q is taken and dissolved in 500 ml; if there should be any turbidity this is filtered off; 50 ml of the solution is treated in exactly the same way as described above, and from the optical density found, the naphthionate content is determined by means of the calibration curve.

The experimental accuracy is characterized by a mean absolute error of ± 0.1% and a maximum error of ± 0.25%.

Determination of the Naphthionic Acid in a Reaction Mass

Control of the first stage of the Bucherer reaction is of practical interest. In this case it is necessary to take into account the presence in the reaction mass (apart from unreacted naphthionic acid) of the bisulfite compound which is colorless and does not react with HNO_2, and of bisulfite which is taken in a twofold excess. Special tests showed that naphtholsulfonic acid was absent.

The presence of bisulfite does not affect the yield of dye. Reproducible and reasonably accurate results are obtained. In the presence of $NaHSO_3$ the scatter in the values of the optical density is of the same order as in its absence.

Determination of the naphthionic acid in the reaction mass can be carried out in the main by the procedure described in the previous section. In this case, however, the standard solutions should contain a known amount of bisulfite instead of naphtholsulfonic acid; in actual practice 50 ml lots of solution were taken containing 0.44 g/liter of $NaHSO_3$. In order to measure the optical density on the TsZ-A apparatus it is expedient to dilute the dye solutions 10 times. In constructing the curve in this case it is more convenient to plot the concentration (in the undiluted solution) of the dye in mole/liter along the abscissa. The curve (Fig. 2) is appreciably curved

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* When a FÉK-M apparatus is used with a cuvette whose length is 10 mm there is no need to dilute.

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DETERMINATION OF THE EXCHANGE CAPACITY OF ION EXCHANGE RESINS BY THE ISOTOPE DILUTION METHOD

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Recently, several authors [1] have suggested the use of the isotope dilution method for determining the value of the toal ion exchange capacity of ion exchange resins. The use of this method is particularly expedient for studying natural sorbents. Actually, natural ion exchange resins of the clay type readily form colloidal solutions. As a consequence of this, the capacity of such sorbents cannot be found either on the basis of the elution curve or on the basis of the adsorption isotherm. The insufficient stability of ion exchange resins – which are aluminosilicates or humates – with respect to concentrated solutions of acids or alkalis, excludes the possibility of converting the sorbent into the H^+ or OH^- forms, as a result of which determination of the capacity of acid-base titration is impossible. As for establishing the capacity of aluminosilicates by chemical analysis, this is out of the question in the case of certain elements, since it is not known which part of the ions enter into the aluminosilicate skeleton of the sorbent and which part is found in the ion exchange state.

Determination of the capacity of a sorbent by the ion exchange method, or, more accurately by the method of isotope dilution consists of the following: A certain amount of the ion exchange resin in a definite form, (i.e., associated with a certain element or group) is placed in a solution containing the isotope of the same element in the form of which the sorbent is found. As a result of isotopic exchange, in which only the ions which are capable of being exchanged participate, the specific activity of the solution decreases. When a state of equibibrium has been reached, the specific activities of the element in solution and in the sorbent are the same, and the value of the exchange capacity of the sorbent can be calculated by means of the formula:

$$S = (k - 1) \cdot b/p,$$

where S is the value of the total exchange capacity of the sorbent in mg-equivalents/g; k is the ratio of the initial radioactivity of the solution to the final radioactivity, b is the content of the element in the whole volume of the solution in mg·equivalents, and p is the weight of the sorbent in g.

The capacity of various samples of soils and earths established by a colloidal-chemical method and by the isotope dilution method is almost the same [2].

Our aim was to determine the capacity of certain natural and synthetic ion exchange resins by the isotope dilution method, and to compare the results obtained with the result of a direct acid – base titration (Table 1). The cation exchange resins KU-2 and wofatite KS were used as test materials.

Aliquots of the sorbents in the hydrogen form were titrated with $Ca(OH)_2$ using phenolphthalein as an indicator. As a result of this, the resins were converted into the calcium form, and the capacity of the resins calculated on the basis of the titration results obtained. Subsequently, the same samples of resin were brought into contact with 50 ml of a solution of $Ca(NO_3)_2$ containing Ca^{45} and having a pH of 9. A state of equilibrium was attained in 3-6 hours.

By finding the ratio of the initial radioactivity of the solution to its equilibrium radioactivity, the coefficient K is determined, and knowing this, the exchange capacity of the resin was calculated.

TABLE 1

Exchange Capacity of the Cation Exchange Resins KU-2 and Wofatite KS, as Determined by Titration and by the Isotope Dilution Method

Cation exchange resin	Wt. of sorbent, g	Capacity of the resin, mg · equivalents/g, as determined by:	
		titration	isotope dilution method
KU-2	0,100	3,98	3,92
»	0,150	3,98	3,91
»	0,300	4,04	3,95
		Mean 4,00	3,93
Wofatite KS	0,200	2,56	2,54
»	0,305	2,58	2,53
»	0,601	2,54	2,48
		Mean 2,56	2,53

TABLE 2

Determination of the Exchange Capacity of Glauconite and Montmorillonite by the Isotope Dilution Method

Sorbent	Wt. of sorbent, g	Capacity, mg. equivalents/g
Glauconite	2,000	0,153
»	2,000	0,156
»	2,000	0,154
		Mean 0,154
Montmorillonite	0,500	0,497
	1,000	0,499
»		
		Mean 0,498

The isotope dilution method permits a fairly accurate determination of the capacity of ion exchange resins (Table 1). We used this method for determining the exchange capacity of some natural ion exchange resins-glauconite from the Voskresenskii Chemical Combine and montmorillonite from the Brayanskii deposit (Czechoslovakia). The capacity of the glauconite was determined by means of cesium and that of the montmorillonite was determined with the aid of calcium. In order to convert the sorbents into the appropriate forms, aliquots of these sorbents were successively treated with solutions of the corresponding salts in such a way that the solution after treatment of the first aliquot of sorbent was then used for treating another aliquot, etc. Montmorillonite was treated under static conditions, and glauconite was converted into the cesium form in columns. Each of the samples was then carefully washed with water to remove excess salt and was subjected to isotope exchange by the technique described above. In those cases where the calculated values of the capacity of the sorbents agreed for all the samples, it was possible to assume that the sorbent was completely converted into the appropriate form, and that the results found correspond to the values of the total exchange capacity of the sorbents.

The values of the exchange capacity of all the samples of glauconite and montmorillonite tested agreed satisfactorily (Table 2).

The isotope dilution method coupled with the use of ion exchange resins can also be applied for determining the concentration of ions containing radioactive isotopes in solution. For this purpose it is necessary both to use an ion exchange resin which has been converted into the form corresponding to the form present in solution, and to ensure that capacity of the ion exchange resin will be determined carefully. Then, by solving the equation given above with respect to b, the content of the test ion in the total volume of solution is found:

$$b = PS/(k - 1),$$

where p and S are known values while k is determined experimentally.

This method is not applicable when the test solution contains ions which are capable of being competitively sorbed by the resin. At the same time, this method makes it possible to avoid gravimetric analysis during investigations of highly active solutions, while the use of sorbents with a small capacity presumably could permit determination of small amounts of materials without their preliminary concentration.

SUMMARY

Results of the determination of the exchange capacity of ion exchange resins by the isotope dilution method and by direct acid – base titration of the resins in the hydrogen form show satisfactory agreement.

The isotope dilution method has been used for determining the exchange capacity of natural ion exchange materials, glauconite, and montmorillonite.

The isotope dilution method coupled with the use of ion exchange resins can be applied for the analytical determination of ions containing radioisotopes in solution.

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POTENTIOMETRIC DETERMINATION OF RHENIUM IN THE PRESENCE OF MOLYBDENUM

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Quantitative determination of rhenium is almost always connected with its separation from molybdenum. Although a fair amount of work has been published on the separation of rhenium from molybdenum, information about the possibility of a quantitative determination of rhenium in the presence of molybdenum is very scant [1, 2, 7].

A method which we have developed permits determination of rhenium in the presence of small amounts of molybdenum (Re : Mo about 1 : 1). The method is based on titration of perrhenate with solutions of divalent chromium using a platinum indicator electrode. The choice of the indicator electrode and medium was made on the basis of the work of A. I. Busey and Li Gyn, who showed that molybdenum, during chromometric reduction, does not give a potential jump Mo^{V}/Mo^{III} in sulfuric acid media on a platinum indicator electrode, [3].

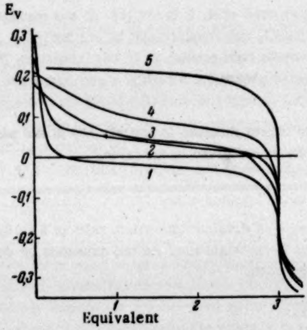

Fig. 1. Reduction of perrhenate with a $CrSO_4$ solution in a sulfuric acid medium. 1) 1 N H_2SO_4; 2) 4.5 N H_2SO_4; 3) 9 N H_2SO_4; 4) 12 N H_2SO_4; 5) 15 N H_2SO_4. The potential values are given relative to the saturated calomel electrode.

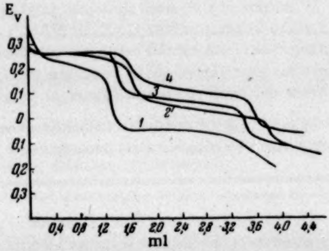

Fig. 2. Potentiometric titration of rhenium with $CrSO_4$ in the presence of molybdenum. 1) 1 ml of 0.0522 M $HReO_4$ equivalent to 9.71 mg Re taken; $N_{H_2SO_4} = 1$; $N_{CrSO_4} = 0.0800$; the potential jump occurred at 3.30 ml − 1.28 ml = 2.02 ml. 2) 9.71 mg Re; $N_{H_2SO_4} = 4.5$; $N_{CrSO_4} = 0.0680$; the potential jump occurred at 3.80 − 1.62 ml = 2.18 ml. 3) 9.71 mg Re; $N_{H_2SO_4} = 9$; $N_{CrSO_4} = 0.0814$; the potential jump occurred at 3.40 − 1.35 ml = 2.05 ml. 4) 9.71 mg Re; $N_{H_2SO_4} = 12$; $N_{CrSO_4} = 0.0784$; the potential jump occurred at 3.50 − 1.55 ml = 1.95 ml. The potential values are given with respect to the saturated calomel electrode.

TABLE

Determination of Re in the Presence of Mo

Re			Mo
taken, mg	found, mg	error, mg	taken, mg
9.71	9.30	- 0.41	11.32
7.77	7.90	+ 0.13	11.32
12.62	13.00	+ 0.38	11.32

Reduction of perrhenate by a solution of a divalent chromium salt is illustrated by the titration curves (Fig. 1). Under these conditions, the perrhenate is reduced to quadrivalent rhenium. As one might expect in accordance with Nernst's equation (for the given reaction: $ReO_4^{-1} + 4H^+ + 3e = ReO_2 + 2H_2O$), with increasing acidity, the reduction potential changes from +0.234 (with respect to the hydrogen electrode) in 1 N H_2SO_4 to +0.461 in 15 N H_2SO_4. During reduction of perrhenate, intensely colored, brown, transparent, colloidal solutions of $ReO_2 \cdot nH_2O$ are obtained in all cases. On increasing the acidity further (above 15 N H_2SO_4) reduction of sulfuric acid by the divalent chromium ions occurs.

In the course of establishing the conditions for the quantitative determination of rhenium in the presence of molybdenum, it was found that the sharpest potential jump on completion of the reduction of Re^{VII} to Re^{IV} is observed at a sulfuric acid concentration of 4 N and higher, at a temperature of 60-70° (Fig. 2). At H_2SO_4 concentrations in excess of 12 N, the rate at which the potential is established on the platinum electrode slows down. Accordingly, to determine rhenium quantitatively in the presence of molybdenum, it is best to carry it out in the H_2SO_4 concentration range 4 N to 12 N.

A solution of a divalent chromium salt was prepared by the method of A. I. Busev [4]. It was standardized and checked by titration with $CuSO_4$ in HCl 1 : 1 at 25° [5]. The $CuSO_4$ was standardized by electrolysis. All the experiments were carried out in a small, thermostatted cell, constructed previously in our laboratory [6]; the experiments were carried out in a nitrogen atmosphere. The potentials were measured by a compensation method on a Leeds and Northrup potentiometer.

By observing the conditions indicated above, it is possible to titrate rhenium quantitatively in the presence of molybdenum by chromometric potentiometric titration. The results are given in the table.

SUMMARY

A study has been made of the reduction of perrhenate by means of divalent chromium salts in a sulfuric acid medium using a platinum indicator electrode; conditions have been established for the quantitative determination of rhenium in the presence of small amounts of molybdenum.

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*Original Russian pagination. See C. B. Translation.

LUMINESCENT DETERMINATION OF SMALL AMOUNTS OF ALUMINUM IN METALLIC MAGNESIUM

A. F. Fioletova

The method for determining small amounts of aluminum is based on its extraction as the 8-hydroxyquinolate with chloroform, and comparing the fluorescence of the extract with that of a standard. Such a method has already been used for the determination of aluminum [1-3].

The optimum intensity of the fluorescence develops within a few minutes, and remains unchanged for 24 hours; subsequently, the intensity gradually increases.

NO_3^- and SO_4^{2-} ions do not interfere whatever their concentration. Trivalent iron interferes (it extinguishes the luminescence) should there be 1×10^{-5} g or more of it present per ml of solution. Ca and Cr do not interfere even when 1×10^{-2} g of these elements is present per ml of solution. Magnesium approximately halves the intensity of the fluorescence. Accordingly, it is necessary to add the same amount of magnesium to the standard solution as there is of magnesium present in the test solution; or to use the chloroform extracts from the test solution after the aluminum has been extracted for preparing the standard solution. The latter technique appeared to be the best method.

The following reagents are required for determination of Al in magnesium metal:

1) hydrochloric acid distilled in a quartz apparatus;

2) a solution of 80 g of $NaHCO_3$ in 1 liter; the latter was purified from aluminum by shaking it with a 2% solution of 8-hydroxyquinoline and $CHCl_3$ containing 0.8 g $NaHCO_3$ in 10 ml;

3) a 2% solution of hydroxyquinoline in 1 N CH_3COOH (2 g of pure 8-hydroxyquinoline + 6 ml of glacial acetic acid in 100 ml);

4) chloroform, distilled in a quartz apparatus and checked for absence of fluorescence.

Procedure. An amount equaling 0.2000 g of magnesium metal, accurately weighed, is placed in a 50 ml quartz breaker. It is moistened with approximately 5 ml of water and then carefully dissolved in 6 N HCl, the latter being added dropwise (spluttering). The solution is evaporated on an electric hotplate covered with an asbestos sheet until it has a syrupy consistency. After cooling, the contents of the beaker are dissolved in 6 N HCl and then transferred to a 50-ml quartz separating funnel; 10 ml of pure diethyl ether is added and the whole vigorously shaken for 3-5 minutes; after standing for ten minutes the aqueous phase is poured into the same beaker from which it was taken, and the ether is transferred into another beaker which contains a few crystals of KSCN and 1 ml of water. The operation is repeated until there is no reaction for Fe in the ether extract.

After removal of Fe, the solution in the quartz beaker is again evaporated to the consistency of a syrup on cooling, the residue is dissolved in water and the solution transferred to a 200-ml quartz flasks. The separating funnel and beaker are washed with water and the washings added to the contents of the 200-ml flask. The solution is finally made up to the mark with water and mixed.

10 ml of this solution is pipetted into a quartz separating funnel and 1 ml of the $NaHCO_3$ solution added [2]. Solutions prepared in this way usually have a pH of about 7 (check by universal indicator). 1 ml of 2% 8-hydroxyquinoline and 5 ml of chloroform are added and the contents of the flask vigorously shaken for 5 minutes, and then allowed to stand for 5 minutes. The chloroform layer is poured into a 10-ml quartz tube, and the extraction repeated with $CHCl_3$, the chloroform layer is combined with the first chloroform extract in the tube; the volume is finally made up to the mark with chloroform and the whole thoroughly mixed.

TABLE

Sample	Weight taken, g	Al found, %			Mean, %
		determination			
		1	2	3	
1567	0,2000 in 200ml solution	0,002	0,002	0,002	0,002
MD-1	0,2000 in 200 » »	0,004	0,004	0,004	0,004
MD-2	0,2000 in 200 » »	0,001	0,002	—	0,0015
MD-3	0,0500 in 50 » »	0,003	0,003	—	0,003
MD-4	0,2000 in 200 » »	0,003	0,004	—	0,0035

At the same time, into another similar separating funnel, 10 ml of water and a standard solution containing approximately the same amount of aluminum that is expected in the test material are introduced. After carrying out the same extraction procedure for aluminum as was used for the test solution the extracts obtained are compared in UV-light (HQS-500 lamp) in order to choose the standard more carefully. In order to get accurate results the amount of Al found is added to the test solution of magnesium from which the aluminum has been removed, and the hydroxyquinolate of aluminum extracted with chloroform as indicated above. When the intensity of the fluorescence does not coincide, choice of standards is repeated until the intensity of the fluorescence does coincide. The percentage of aluminum in the sample is calculated by means of the formula: $\% \text{ Al} = a \cdot 100/0.1$, where $\underline{a}$ is the amount of Al found in 10 ml of solution.

Results for determination of aluminum are given in the table.

Using standard solutions it has been shown that it is possible to determine 0.00001% Al, but the method requires considerable time and gives an error of 20%. Under such conditions it is necessary to purify the reagents more carefully from Al and Fe.

SUMMARY

For the determination of aluminum present as an impurity in magnesium metal, a method is suggested in which the intensity of the fluorescence of a chloroform extract of aluminum hydroxyquinolate is measured.

Determination of thousandths of a percent of aluminum in magnesium metal can be carried out with an accuracy of ± 14%.

Two samples can be analyzed in duplicate in six hours by one analyst.

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DETECTION OF ALUMINUM IONS BY MEANS OF 5-HYDROXY-1,4-NAPHTHOQUINONE (JUGLONE)

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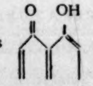
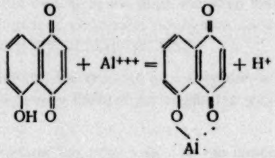
Kuznetsov [1] considers that the group of atoms  is a functional analytical group for Al^{3+}. The capacity to form colored lakes with Al^{3+} is determined by the presence of a phenolic hydroxyl (salt-forming group) and a complex-forming carbonyl in the ortho or para position with respect to this hydroxyl group [2]. A description is given in the present article of a method for detecting aluminum by means of juglone, 5-hydroxy-1,4-naphthoquinone which was synthesized by L. N. Aizenberg's method [3]. The method is based on the formation of a purple-colored inner complex compound of aluminum with juglone in an ammoniacal medium. In practice the reaction is carried out as a spot reaction and also as a macro reaction. In the first instance the technique for carrying out the spot test is similar to that used for the reaction with alizarin [4].



Detection of aluminum in mixtures with other ions is possible in the presence of $K_4[Fe(CN)_6]$ (a saturated solution) which forms sparingly soluble ferrocyanides with the cations of the other elements. A drop of a saturated solution of potassium ferrocyanide is placed on a filter paper. This is followed by a drop of juglone solution; the paper is treated with ammonia vapor and a drop of the test solution added.

In the presence of copper ions, which also form a dark-red colored compound with juglone, 0.5 ml of a solution of a mixture of cations is treated with metallic zinc in order to remove the ions of copper and other heavy metals, and the test tube shaken for 2 minutes. A drop of the clear solution is taken out with a capillary and any aluminum present detected by means of juglone as described above. In the presence of ferrous and ferric ions a brown spot is formed. However, for a weight ratio of $Fe^{3+} : Al^{3+}$ of 2 : 1, it is still possible to detect 0.16 mg Al^{3+} when five drops of test solution are used.

Ni^{2+} and Zn^{2+} even in large excess do not interfere with the red color characteristic for aluminum.

On mixing solutions of aluminum salts (10^{-1} M) with a pH of 2.3-3.5 with an alcoholic solution of juglone (3.44×10^{-3} M) in a test tube, a red color appears which increases on shaking and attains a maximum intensity after several minutes.

At concentrations of the aluminum salts less than 2.5×10^{-3} M the red color does not appear. The most intense red color is observed for a ratio of the volumes of the solutions of the aluminum salts and juglone of 2.5 : 7.5.

The limit of identification is 162 γ of Al^{3+} in 2 ml of $Al(NO_3)_3$ solution. The limiting dilution is 1: 24,000.

The red color of the compound of aluminum with juglone is brightest at a pH of 3.0-3.5 for $AlCl_3$ and at a pH of 2.25-9.90 for $Al(NO_3)_3$.

Trivalent chromium ions give a green color with a 3×10^{-3} M solution of juglone, Fe^{3+}, a blood red color; Ni^{2+}, a yellow-brown (color of tea); Co^{2+}, a light orange color; Cu^{2+}, a red color; Ce^{3+} an orange-red color. The latter, in the presence of NH_3, gives with juglone exactly the same red color on paper as Al^{3+}. Ca^{2+}, Sr^{2+} Ba^{2+}, Na^{+}, K^{+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Bi^{3+}, Sn^{2+}, Sb^{III}, Ag^{+} do not lead to an intensification of color with a juglone solution.

SUMMARY

A spot reaction for Al^{3+} with juglone is described. The sensitivity and limiting dilution of the reaction have been established. The effect of pH and of certain metal cations on the formation of the compound of aluminum with juglone has been studied.

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POLAROGRAPHIC STUDIES OF TITANIUM AND NIOBIUM IN PYROPHOSPHORIC ACID SOLUTIONS

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A number of authors have carried out separate polarographic studies of titanium and niobium, in solutions of mineral acids and in solutions of certain organic complexing agents. Recently [1, 2] it has been indicated that it is possible to obtain waves for titanium and niobium in eachother's presence in sulfuric acid solution (70% H_2SO_4). However, Ya. P. Gokhshtein [3] has shown that under these conditions, the niobium wave is distorted by the hydrogen wave. Results of such work cannot therefore be used for the quantitative polarographic determination of titanium and niobium in each other's presence.

In developing a simple method for the determination of these elements we carried out a polarographic study of titanium and niobium in a pyrophosphoric acid medium.

Solutions of titanium and niobium in concentrated pyrophosphoric acid (sp. gr. 1.85) were used in the course of the work. Pyrophosphoric acid solutions of titanium and niobium were prepared as follows: an aliquot of the appropriate oxide was used with potassium bisulfate; the melt was then leached with sulfuric acid. The hydroxide was precipitated from this solution by means of ammonia; the hydroxide was filtered off through a glass filter, and, after washing, dissolved in pyrophosphoric acid, sp. gr. 1.85.

It was found that titanium and niobium are reduced on a dropping mercury cathode in a supporting electrolyte of pyrophosphoric acid, and give clearly defined polarographic waves both when taken separately and together (Fig. 1).

The curve drawn within the coordinates log i (i_d - i), E in the concentration range 1 to 50 millimoles/liter showed that the value of the reciprocal tangent of the slope of the lines for titanium, taken on its own, or together with niobium, had a value close to that expected from the equation for the wave $E = E_{1/2} - RT/nF \ln i/(id-i)$ for a one-electron, reversible process. In the case of niobium the value of the slope coefficient varies from 0.058 to 0.080. On this basis the reduction process can be represented by the following equations:

$$Ti^{IV} + e \rightleftarrows Ti^{III}; \; Nb^{V} + e \rightarrow Nb^{IV}$$

The half-wave potentials for titanium and niobium are respectively 0.145 and 0.520 with respect to the saturated calomel electrode.

The limiting current of titanium and niobium, taken separately, or together, up to a ratio of Nb:Ti = 1 : 20 is directly proportional to their concentration in solution (Fig. 2).

The linear relationship between limiting current and concentration, coupled with the appreciable difference between the half-wave potentials for these two elements, and the clearly defined waves for titanium and niobium means that it is possible to determine these two elements in eachother's presence. Results of such determinations are given in the table.

It should be noted that solutions of titanium and niobium in pyrophosphoric acid are stable for several months and give readily reproducible polarograms.

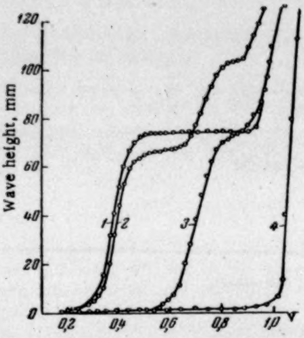

Fig. 1. Polarographic waves for titanium and niobium in pyrophosphoric acid sp. gr. 1. 85). 1) Titanium, 10.7 millimole/liter; 2) titanium, 9.4 millimole /liter and niobium 6.25 millimole/liter in each others presence; 3) niobium, 13.35 millimole /liter; 4) supporting electrolyte pyrophosphoric acid sp. gr. 1.85; T = 25°, $P = m^{2/3} \cdot \tau^{1/6} = 0.94$ $mg^{2/3}$ $sec^{-1/2}$; galvanometer sensitivity 1/3; anode — internal.

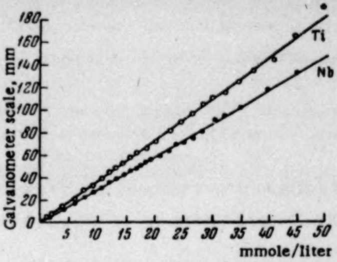

Fig. 2. Relation between the limiting current of titanium and niobium and their concentration in solution. Concentration in millimole/liter: $P = m^{2/3} \cdot \tau^{1/6} =$ 0.94 mg $^{2/3}$ $sec^{-1/2}$, galvanometer sensitivity 1/5.

SUMMARY

The polarographic behavior of titanium and niobium in pyrophosphoric acid (sp. gr. 1.85) has been studied for the first time. It has been shown that titanium and niobium are reduced and give clearly defined polarograms, when these elements are taken either separately or together.

The appreciable difference between the half-wave potentials of titanium and niobium, and the linear relationship between their limiting current and their concentration in solution permits them to be determined in each other's presence up to a ratio of Nb: Ti = 1:20.

Polarographic Determination of Titanium and Niobium in Each Other's Presence

Taken, mmole/l		Found, mmole/l		$C_{Ti} : C_{Nb}$	Taken, mmole/l		Found, mmole/l		$C_{Ti} : C_{Nb}$
Ti	Nb	Ti	Nb		Ti	Nb	Ti	Nb	
17,7	0,90	17,6	0,9	18,6	4,65	18,9	4,5	18,1	0,25
16,45	1,0	16,5	0,95	16,5	5,4	25,0	5,6	24,2	0,21
17,25	1,41	17,3	1,39	12,2	14,9	15,0	14,5	15,2	1
12,9	1,59	13,0	1,59	8,1	—	2,15	—	2,15	—
7,42	1,83	7,5	1,80	4,1					

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*Original Russian pagination. See C. B. Translation

A SPOT METHOD FOR THE DETECTION OF MICRO AMOUNTS OF BORON IN SILICON

A. L. Sokolova and N. A. Makharashvili

The method is based on a change in the color of curcumin in an acid medium from yellow to red in the presence of boron.* Detection is carried out on a filter paper impregnated with a 1% tincture of curcumin. The method permits determination of 0.05 γ of boron in 0.05 ml of solution. The high sensitivity is achieved [1] by concentrating the test solution on the paper surface on which paraffin rings have been placed.**

An amount equaling 0.1-1 g of silicon in the form of a finely ground powder is dissolved in 5-10 ml of 10% sodium hydroxide on a water bath. The solution obtained is evaporated to dryness. To the dry residue is added 2 ml of 1 N sulfuric acid, the solution is cooled with ice and 3 ml of concentrated sulfuric acid and 40 ml of purified methanol added. The mixture obtained is transferred to a distillation flask [2] for distilling off the methyl*** ester of boric acid. Saponification of the ester is carried out in a flask (in the receiver) with a mixture of 1 ml of 5% NaOH and 8 ml of methanol. When the methyl ester has been distilled off, the solution in the new flask is evaporated to dryness on a water bath. The cooled residue is dissolved in 5-10 drops of HCl (1 : 1) and a few drops of a saturated solution of oxalic acid added. The total volume of the solution should not exceed 1 ml. The solution **** obtained (0.01-0.05 ml) is placed on the filter paper inside the paraffin ring and the paper then dried in a desiccator over calcium chloride. The color is compared with that of a series of standards prepared at the same time; these standards are prepared as follows: into a small quartz basin is poured 1 ml of a solution of boric acid of known concentration (from 1γ to 10 γ), 1 ml of a 5% solution of sodium hydroxide, and 5 ml of methanol are added. The contents of the basins are evaporated to dryness on a water bath; the dry residues are then dissolved in hydrochloric acid (1 : 1) and oxalic acid added. The solutions obtained are placed on filter papers prepared beforehand and the latter dried in a desiccator. The sensitivity of the method is 0.05 γ of boron in 0.05 ml of solution (1 : 1,000,000). In view of the fact that it is difficult to transfer the test solution (0.5 ml or 1 ml) completely onto the paper, boron can only be determined by this technique up to a limit of 2×10^{-6} g/g.

For increasing the sensitivity of the determination of boron in silicon it is recommended that: a) the diameter of the ring be increased from 0.5 cm to 2 cm; b) the volume of test solution applied to the paper be increased (from 0.01 ml to 0.5 ml); c) the amount of silicon taken be increased to 1 g.

SUMMARY

A simple method has been developed for the determination of up to 10^{-6} g/g of boron in silicon by means of a spot test with curcumin on filter paper.

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*When the red color of curcumin is caused by the presence of boron, on addition of alkali, the color changes to green.

**The paraffin rings are placed on a filter paper soaked with curcumin by means of a heated glass tube (internal diameter 1 cm, external diameter 2 cm).

***When 0.1 to 0.25 g of silicon is taken, separation of boron from silicon is carried out with methanol without distillation.

****The test solution is placed on the filter paper by means of a microburet, the tip of which has been drawn out into a fine capillary.

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ANALYSIS OF PENTABORANE

A. F. Zhigach, E. B. Kazakova and R. A. Kigel'

A long method for analyzing pentaborane has been described in the literature [1], it is based on its decomposition into boron and hydrogen at 700-800°. This method requires the use of a high vacuum setup. We have developed a more rapid and simple method of analyzing pentaborane which is based on the capacity of the latter to react with ethanol with liberation of hydrogen and formation of $B(OC_2H_5)_3$ [2]; the latter is readily hydrolyzed by water to give boric acid:

$$B_5H_9 + 15C_2H_5OH \rightarrow 5B(OC_2H_5)_3 + 12H_2, \qquad (1)$$

$$5B(OC_2H_5)_3 + 15H_2O \rightarrow 5H_3BO_3 + 15C_2H_5OH \qquad (2)$$

From the volume of hydrogen liberated and which is measured, and from the amount of boron determined on the basis of boric acid, the composition of the pentaborane samples can be determined.

Experimental Procedure. The test sample of pentaborane is stored in flask A with two taps 1 and 2 and a tube (Fig. 1). When a sample is taken, nitrogen is passed through tap 1 in order ot prevent the pentaborane from coming into contact with air.

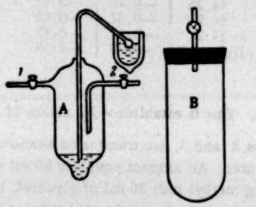

Fig. 1.

Decomposition of the sample of pentaborane is carried out in vessel 1, (Fig. 2)which has a capacity of 50 ml and is provided with a funnel, two taps, and a tube. Vessel 1, is connected with two absorption flasks 2, and 3, with a capacity of 40 ml, into each of which 20 ml of 96% ethanol is introduced. These absorption flasks are connected in turn with gas burets 4 and 5, (the first has a capacity of 100 ml and is accurately graduated, and the second has a capacity of 500 ml). The gas burets and the leveling flasks are filled with ethanol. Before carrying out an analysis it is necessary to sweep out the apparatus carefully with nitrogen; an ampoule containing the test material is placed in vessel 1 which is then sealed with a stopper into which a "crusher" (for breaking the ampoule) has been fitted beforehand. Vessel 1 is connected with flasks 2 and 3, an amount equaling 10 ml of ethanol is poured into the funnel, and the ampoule is broken. Vessel 1 is immersed in ice water and alcohol is slowly added. The reaction proceeds very vigorously initially. It subsequently slows down and finishes completely in 1.5 2 hours. As soon as all the alcohol has been added, cooling is stopped and subsequent operations are carried out at room temperature.

During an analysis, the pressure in the system should be about 10-12 mm Hg below atmospheric in order to prevent a breakthrough of the gas through the tap of the funnel in vessel 1. If there should be a breakthrough, the determination must be repeated. The volume of the hydrogen liberated is measured when the position of

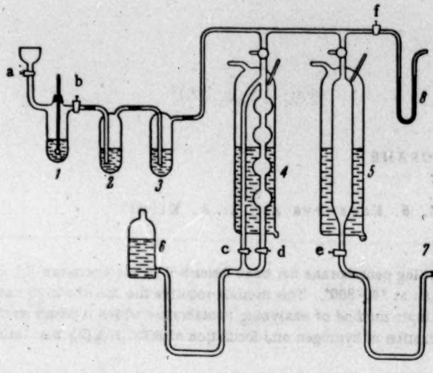

Fig. 2.

TABLE

Analysis of Pentaborane Samples(Calculated for B_5H_9, 85.64% B, 14.36% H)

Sample, weight, mg	Calculated		Determined				Relative accuracy	
	B	H	B, mg	H, ml	B, %	H, %	B, %	H, %
122,0	104,4	519	104,1	518,5	85,3	14,3	−0,4	−0,42
149,6	128,1	636,5	127,5	637,0	85,2	14.37	−0,52	+0.01
85,9	73,5	365,5	73,5	364,4	85,6	14,3	−0,04	−0,42
143,4	122,8	610,2	122,8	606,8	85,6	14,28	−0.04	−0,56
129,0	110,4	548,8	110,0	550	85,3	14,3	−0,4	−0,42
133,6	114,4	568,4	113.6	564,5	85,0	14,25	−0.75	−0,77
140,4	120,2	598,9	119,5	596	85,5	14,3	−0,57	−0,42
130,3	112,1	556,9	111,8	552,4	85.3	14,2	−0,4	−0,42
					Mean value		−0,30	−0,48

the alcohol levels in the burets and the leveling flasks are the same. This is established by means of manometer 8.

To determine boron, the solutions from vessel 1, and from traps 2 and 3, are transferred quantitatively into a 250 ml standard flask and the volume made up to the mark with water. An amount equaling 50 ml of this solution is taken for titration; it is neutralized with 0.1 N alkali using methyl red; 30 ml of glycerol, invert sugar or mannite is added, followed by a few drops of phenolphthalein, and the mannite-boric acid titrated to the appearance of a rose color.

The pentaborane is sampled in 0.5 ml glass ampoules. In order to take samples, the ampoules which have been drawn out at an angle are weighed and then placed in tube B (Fig. 1), and the latter hermetically sealed. A vacuum is set up in the tube after which it is filled with nitrogen. Evacuation and filling with nitrogen is repeated twice. An ampoule is withdrawn from tube B and its capillary introduced into vessel A containing the test pentaborane. A 5 ml Dewar flask containing a cooling mixture of acetone and solid carbon dioxide is placed under the bulb of the ampoule. When the ampoule is half full, the capillary is lifted so that its tip is above the liquid level. Two fingers are drawn along the capillary from its bulb to the tip in order to free it (as a result of warming up) from liquid, and it is then rapidly sealed over an alcohol burner; the ampoule is finally weighed. The weight of sample taken amounts to 0.1 to 0.2 g.

The analytical results obtained are given in the table.

The accuracy of the method was checked by analyzing pure pentaborane (bp equals 60.0-60.2° at 760 mm mp equals-46.50°).

Found, %: B 85.5; H 14.3

B_5H_9 Calculated, %: B 85.64; H 14.36

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SEPARATION OF THE ISOMERIC PHTHALIC ACIDS BY PARTITION PAPER CHROMATOGRAPHY

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For qualitative separation of mixtures of terephthalic and isophthalic acids we have used the method of ascending partition chromatography on paper using concentrated aqueous solutions of alcohols miscible with water, and using bromothymol blue as an indicator for identifying the components of the mixture.

Mixtures were made from 0.1 N solutions of terephthalic and isophthalic acids in pyridine redistilled at 115°. The chromatograms were taken on paper from the Volodarskii No. 2 Leningrad Factory. The density of the paper was 85 g/meter^2 Mark B (rapidly absorbent).

Using a micropipet, 0.05 ml drops of the test solutions were placed on paper strips 260 x 60 mm in size on which a line had been pencilled at a distance of 30 mm from the lower edge of the starting line, and on which circles had been pencilled at the points where the drops of the test solutions were to be applied (these circles were at distances of 30 mm from each other, and 15 mm from the side edges of the paper). After the paper strips had been dried in air, they were placed in a chromatographic tank on the bottom of which had been placed a vessel containing solvent consisting of a mixture of 350 parts of propyl alcohol, 12 parts of 3.5% ammonia, and 105 part of water. The solvent front was allowed to run for 10 to 15 hours. When the chromatograms had been run, they were removed from the tank and dried in a drying oven at 40-50° or in air, after which they were sprayed with an aqueous solution of bromothymol blue whose pH had been adjusted to 8 beforehand with alkali. An atomizer was used for the spraying.

TABLE

Acid solution placed on the chromatogram	Partition coefficient R_f		
	reference	mixture of acids	
		terephthalic acid	isophthalic acid
Terephthalic acid	0.20; 0.15; 0.17	–	–
Isophthalic acid	0.33; 0.46; 0.49	–	–
Mixture of acids	–	0.21; 0.15; 0.17	0.34; 0.46; 0.50

On the damp chromatograms, yellow spots with sharply defined contours appeared on the blue background. These spots were outlined with a slate pencil. This is necessary, because during subsequent drying of the chromatograms in air, under a vacuum, or in a drying oven at 40-50°, the color of the background changes from blue to a bright-yellow.

The test chromatogram was then placed on the light filter of a UB-1 utrachemiscope and firmly pressed against the fluorescent screen. On the latter, at those points which were opposite the places on the paper where the test materials had accumulated, and which absorb the ultraviolet, shadows appeared.

The R_f values agree satisfactorily between themselves.

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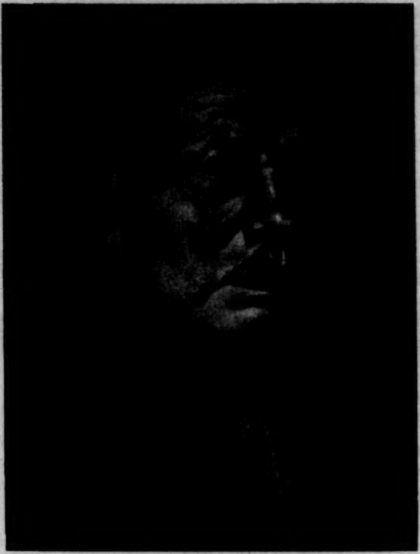

NIKOLAI ALEKSANDROVICH TANANAEV

The death of Professor Nikolai Aleksandrovich Tananaev occurred on June 7th, 1959. He was 82 at the time and an outstanding scientist, a devoted servant of science, a member of the Commission on Analytical Chemistry, the head of the chair of analytical chemistry in the Ural Polytechnical Institute since 1938, and a doctor of chemical sciences.

N. A. Tananaev was born in 1878 in the village of Serp, formerly in Tambovskii province in a peasant family. On finishing in the Tambovskii Seminary, he proceeded to Yur'evskii (Derptskii) University to enter the chemical section of the physicomathematical faculty. In 1903 his studies were interrupted; he was arrested for his part in the revolutionary students' movement. He was exiled until the amnesty of 1905.

Tananaev was only able to continue his further education in 1908. In September of that year he successfully finished his course at Yur'evskii University with a degree of Candidate of Chemistry, and stayed on at the University. In the same year, however, he was invited by L. V. Pisarzhevskii to work in the chemistry faculty of Kiev Polytechnical Institute, where he first worked as a laboratory assistant and subsequently taught quantitative analysis. One result of his scientific and teaching activity during this time was the book "Volumetric Analysis," published in 1913; several editions of this book were published.

His intensive creative work started after the Great October Socialist Revolution. In 1917 he was chosen as a lecturer, and, in 1921, as a professor, in the first chair of analytical chemistry to be organized in the Soviet Union, that of Kiev Polytechnical Institute.

In 1920 Tananaev started to develop the spot method of analysis.

Starting in 1924, Tananaev devoted considerable attention and time to a study of analytical chemical control of production. He published a large number of papers on questions connected with speeding up, simplifying, and developing analytical methods, and also on the introduction of new methods for the chemicoanalytical control of production. These included papers on spot colorimetry, colorimetric titration, special reactions, etc. During this period the methodology of volumetric analysis was developed which foresaw the residues law and the substitution law.

Work on gravimetric analysis occupied no small part in N. A. Tananaev's activity. His experience in this field was collected together in the book: Gravimetric Analysis, (first published in 1931 in Kiev, and subsequently, in the course of the next seven years reissued five times).

Worthy of special mention in his work on the theory of analytical chemistry is his development of the problem of solid phases in chemical analysis. The concept of precipitates as materials which are capable of undergoing further reactions enabled Tananeav to make wide and systematic use of them as reagents. A study of the interactions of precipitates on the basis of the values of their solubility products led to the formulation of the series law, which made it possible to forecast the likelihood of a reaction occurring and how far it would proceed, and thus solve chemicoanalytical and technological problems.

In the course of many years Tananaev worked on the development of qualitative analysis by the "fractional" method (the use of special reagents for each element). The result of this work was the book: Fractional Analysis.

Tananaev was responsible for new, original developments in analytical chemistry: the method of gravimetric express analysis; the spot method; fractional analysis; and the "nondestructive" method (the method in which selected reagents are placed on the material to be analyzed, the latter not being broken up or dissolved in order to analyze it).

Tananaev was the founder of numerous schools for analytical chemists in Kiev and in Sverdlovsk.

Tananaev loved teaching. He payed particular attention to the education of future scientists and tried to attract a large number of students to work in the scientific students' society. The results of his teaching activity are reflected in several textbooks. He published more than 240 papers in all. The books: Spot Analysis, Non-Destructive Analysis and Fractional Analysis have been translated into Czech, Polish, Rumanian, and Chinese.

During the whole of his long life Tananaev actively participated in the social life of the country.

For his successful and fruitful scientific and teaching work, N. A. Tananaev was made an Honorary Worker of Science and Technics of the RSFSR. He was a Stalin Prize winner, and was also awarded orders and medals.

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